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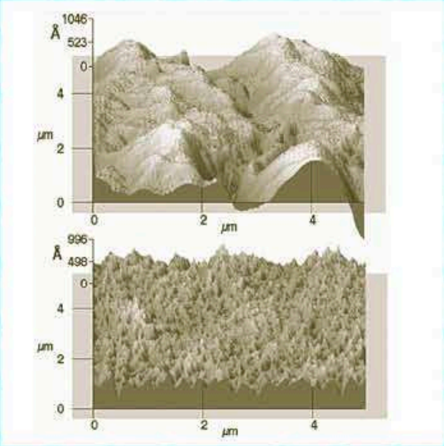

Plasma technologies for textiles

Edited by R. Shishoo

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The Textile Institute

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Plasma technologies for textiles

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Introduction – The potential of plasma technology in the textile industry

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Since their introduction in the 1960s, the main industrial applications of (low-pressure) plasmas have been in the micro-electronic industries. In the 1980s their uses broadened to include many other surface treatments, especially in the fields of metals and polymers. The dominant role of plasma-treated surfaces in key industrial sectors, such as microelectronics, is well known, and plasmas, certainly experimentally and, in places, industrially, are being used to modify a huge range of material surfaces, including plastics, polymers and resins, paper and board, metals, ceramics and inorganics, and biomaterials. Properties enhanced include wettability, adhesion, biocompability, protection and anti-wear, sterilisation, and chemical affinity or inertness. The prospects of very good technical and economical results, as experienced in the microelectronics industry, are stimulating efforts worldwide to apply plasma processing more widely to the processing of textiles and nonwovens. Undoubtedly, tremendous advantages are afforded by plasma technology as a uniquely effective engineering tool for achieving, in a flexible and versatile way, a broad range of functionalisations of textiles and nonwovens.

In the textile field, significant research work has been going on since the early 1980s in many laboratories across the world dealing with low-pressure plasma treatments of a variety of fibrous materials showing very promising results regarding the improvements in various functional properties in plasma-treated textiles. A variety of commercial low-pressure plasma machines, mostly in prototype form, have been offered for batch/in-line processing of textiles for more than 15 years. In recent times, some companies have also started to offer commercial systems for atmospheric-pressure plasma processing of textiles, both in-line and on-line. Despite all the significant benefits demonstrated in the laboratory and industrial prototypes, plasma processing on an industrial scale has been slow to make an impact in the textile industry. This may be due to factors such as important gaps in the relevant applied research, slow development of suitable industrial plasma systems, late focus on developing in-line atmospheric pressure plasma systems and less public transparency regarding the successes and failures of industrial trials.

The textile and clothing industries in Europe, North America and some other developed countries are facing some big challenges today, largely because of the globalisation process. Therefore, the shift to high-functional, added value and technical textiles is deemed to be essential for their sustainable growth. The growing environmental and energy-saving concerns will also lead to the gradual replacement of many traditional wet chemistry-based textile processing, using large amounts of water, energy and effluents, by various forms of low-liquor and dry-finishing processes. Plasma technology, when developed at a commercially viable level, has strong potential to offer in an attractive way achievement of new functionalities in textiles. In recent years, considerable efforts have been made by many plasma technology suppliers to develop both low-pressure and atmospheric-pressure based plasma machinery and processes designed for industrial treatment of textiles and nonwovens to impart a broad range of functionalities.

What are plasmas?

The coupling of electromagnetic power into a process gas volume generates the plasma medium comprising a dynamic mix of ions, electrons, neutrons, photons, free radicals, meta-stable excited species and molecular and polymeric fragments, the system overall being at room temperature. This allows the surface functionalisation of fibres and textiles without affecting their bulk properties. These species move under electromagnetic fields, diffusion gradients, etc. on the textile substrates placed in or passed through the plasma. This enables a variety of generic surface processes including surface activation by bond breaking to create reactive sites, grafting of chemical moieties and functional groups, material volatilisation and removal (etching), dissociation of surface contaminants/layers (cleaning/scouring) and deposition of conformal coatings. In all these processes a highly surface specific region of the material (<1000 Å) is given new, desirable properties without negatively affecting the bulk properties of the constituent fibres.

Plasmas are acknowledged to be uniquely effective surface engineering tools due to:

- Their unparalleled physical, chemical and thermal range, allowing the tailoring of surface properties to extraordinary precision.
- Their low temperature, thus avoiding sample destruction.
- Their non-equilibrium nature, offering new material and new research areas.
- Their dry, environmentally friendly nature.

Plasma reactors

Different types of power supply to generate the plasma are:

Low-frequency	(LF, 50–450 kHz)
Radio-frequency	(RF, 13.56 or 27.12 MHz)
Microwave	(MW, 915 MHz or 2.45 GHz)

The power required ranges from 10 to 5000 watts, depending on the size of the reactor and the desired treatment.

Low-pressure plasmas

Low-pressure plasmas are a highly mature technology developed for the microelectronics industry. However, the requirements of microelectronics fabrication are not, in detail, compatible with textile processing, and many companies have developed technology of low pressure reactors to achieve an effective and economically viable batch functionalisation of fibrous products and flexible web materials.

A vacuum vessel is pumped down to a pressure in the range of 10^{-2} to 10^{-3} mbar with the use of high vacuum pumps. The gas which is then introduced in the vessel is ionised with the help of a high frequency generator. The advantage of the low-pressure plasma method is that it is a well-controlled and reproducible technique.

Atmospheric pressure plasmas

The most common forms of atmospheric pressure plasmas are described below.

Corona treatment

Corona discharge is characterised by bright filaments extending from a sharp, high-voltage electrode towards the substrate. Corona treatment is the longest established and most widely used plasma process; it has the advantage of operating at atmospheric pressure, the reagent gas usually being the ambient air. Corona systems do have, in principle, the manufacturing requirements of the textile industry (width, speed), but the type of plasma produced cannot achieve the desired spectrum of surface functionalisations in textiles and nonwovens. In particular, corona systems have an effect only in loose fibres and cannot penetrate deeply into yarn or woven fabric so that their effects on textiles are limited and short-lived. Essentially, the corona plasma type is too weak. Corona systems also rely upon very small interelectrode spacing (~1 mm) and accurate web positioning, which are incompatible with 'thick' materials and rapid, uniform treatment.

Dielectric barrier discharge (Silent discharge)

The dielectric barrier discharge is a broad class of plasma source that has an insulating (dielectric) cover over one or both of the electrodes and operates with high voltage power ranging from low frequency AC to 100 kHz. This results in a non-thermal plasma and a multitude of random, numerous arcs form between the electrodes. However, these microdischarges are non-uniform and have potential to cause uneven treatment.

Glow discharge

Glow discharge is characterised as a uniform, homogeneous and stable discharge usually generated in helium or argon (and some in nitrogen). This is done, for example, by applying radio frequency voltage across two parallel-plate electrodes. Atmospheric Pressure Glow Discharge (APGD) offers an alternative homogeneous cold-plasma source, which has many of the benefits of the vacuum, cold-plasma method, while operating at atmospheric pressure.

Summary

Cold plasmas can be used for various treatments such as: plasma polymerisation (gaseous monomers); grafting; deposition of polymers, chemicals and metal particles by suitable selection of gas and process parameters; plasma liquid deposition in vaporised form.

Gases commonly used for plasma treatments are:

- Chemically inert (e.g. helium and argon).
- Reactive and non-polymerisable (e.g. ammonia, air, and nitrogen).
- Reactive and polymerisable (e.g. tetrafluoroethylene, hexamethyldisiloxane).

Effect of plasma on fibres and polymers

Textile materials subjected to plasma treatments undergo major chemical and physical transformations including (i) chemical changes in surface layers, (ii) changes in surface layer structure, and (iii) changes in physical properties of surface layers. Plasmas create a high density of free radicals by disassociating molecules through electron collisions and photochemical processes. This causes disruption of the chemical bonds in the fibre polymer surface which results in formation of new chemical species. Both the surface chemistry and surface topography are affected and the specific surface area of fibres is significantly increased. Plasma treatment on fibre and polymer surfaces results in the formation of new functional groups such as —OH, —C=O, —COOH which affect fabric wettability as well as facilitate graft polymerisation which, in turn, affect liquid repellence of treated textiles and nonwovens.

Adhesion problems, especially for synthetic fibre-based fabrics, often arise in coating, bonding and printing of textile materials. The characteristic low surface energy of many polymeric substrates results in intrinsically poor adhesion. Adhesion is fundamentally a surface property, often governed by a layer of molecular dimensions. Many types of wet-chemical surface treatments for adhesion enhancement are becoming increasingly unacceptable because of environmental and safety considerations. Modification of polymer and fibre surfaces by plasma treatment presents many important advantages and offers a great potential as an established means of fabric processing.

In the plasma treatment of fibres and polymers, energetic particles and photons generated in the plasma interact strongly with the substrate surface, usually via free-radical chemistry. Four major effects on surfaces are normally observed. Each is always present to some degree, but one may be favoured over the others, depending on the substrate and the gas chemistry, the reactor design, and the operating parameters. The four major effects are surface cleaning, ablation or etching, cross-linking of near-surface molecules and modification of surface-chemical structure. All these processes, alone or in synergistic combination, affect adhesion. Plasma treatment can be used with great effect to improve the bond strength of polymer to fibre and polymer to polymer combinations. In these cases, the improved adhesion results from both increased wettability of the treated substrate and the modification of surface chemistry of the polymer.

Modified wettability is one of the most apparent results of plasma treatment and the method used for characterising the modification is to measure the advancing and receding contact angles against specific liquids. Plasma-produced polar groups increase the surface free energy, γ, of the fibre and decrease the contact angle, θ, usually correlating with better bonding of adhesives; θ has often been used as an estimate of bonding quality.

Plasmas offer uniquely effective surface engineering tools due to their unparalleled physical, chemical and thermal range, their low temperature (avoiding sample destruction), their dry, environmentally friendly nature, and their nonequilibrium nature offering new material and new research areas.

The advantages of an industrially viable plasma processing system over traditional textile processing are summarised in Table 0.1.

Plasma finishing of textiles

An excellent state-of-the art description of plasma technology and plasma treatment for textiles was presented in six papers in the session on plasma finishing at the TECHTEXTIL – Symposium, May 1997.

Table 0.1 Plasma treatment vs. traditional textile processing

	Plasma processing	Traditional wet chemistry
Medium	No wet chemistry involved. Treatment by excited gas phase	Water-based
Energy	Electricity – only free electrons heated (<1% of system mass)	Heat – entire system mass temperature raised
Reaction type	Complex and multifunctional; many simultaneous processes	Simpler, well established
Reaction locality	Highly surface specific, no effect on bulk properties	Bulk of the material generally affected
Potential for new processes	Great potential, field in state of rapid development	Very low; technology static
Equipment	Experimental, laboratory and industrial prototypes; rapid industrial developments	Mature, slow evolution
Energy consumption	Low	High
Water consumption	Negligible	High

Within the scope of an EU-project LEAPFROG CA, an extensive literature analysis and patent survey was carried out in 2005 in the area of plasmas and plasma-induced functionality of textiles. Hundreds of articles have been written on these subjects and a very large number of patents have been granted in the field of plasma treatment of fibres, polymers fabrics, nonwovens, coated fabrics, filter media, composites, etc. for enhancing their functions and performance. This survey has pointed out the potential use of plasma treatments of fibres, yarns and fabrics for the following types of functionalisation:

- Anti-felting/shrink-resistance of woollen fabrics.
- Hydrophilic enhancement for improving wetting and dyeing.
- Hydrophilic enhancement for improving adhesive bonding.
- Hydrophobic enhancement of water and oil-repellent textiles.
- Facilitating the removal of sizing agents.
- Removing the surface hairiness in yarn.
- Scouring of cotton, viscose, polyester and nylon fabrics.
- Anti-bacterial fabrics by deposition of silver particles in the presence of plasma.
- Room-temperature sterilisation of medical textiles.

- Improved adhesion between textiles and rubber.
- Plasma-treated fabrics with high hydrophilic stability when stored in alkaline media.
- Graft plasma polymerisation for producing fabrics with laundry-durable oleophobic, hydrophobic and stain-resistant finishes.
- Atmospheric plasma-based graft polymerisation of textiles and nonwovens having different surface functional properties on the face and back side of the fabric.
- A fabric which is coated with sizing agent inactive to plasma on one side and on the other side left as hydrophobic or hydrophilic after size removal, the resultant fabric having different functionality on its two sides.
- Flame-retardant coating using monomer vapour (halogen and/or phosphorus) in combination with nitrogen and/or silicone.
- Silicone coating of air-bag fabrics using crosslinked silicone (polyorganosiloxanes).
- Scouring of cotton, rayon, polyester fabrics using a non-polymerisable gas (nitrogen, argon, ammonia, helium), followed by wet treatment for removing the impurities.
- Prevention of readily-occurring colour variation in textiles.
- Durable antistatic properties using PU-resin and plasma processing.
- Shrink resistance of animal hair textiles using urethane-based resin and plasma processing.
- Electro-conductivity of textile yarns by surface plasma deposition.

Plasma systems for experimental and industrial processing of fabrics

Until recently the only available plasma systems for textiles were low-pressure systems designed for batch operation. This type of plasma machinery also exists for ‘air-to-air’ or ‘cassette-to-cassette’, batch–continuous in-line systems for yarn, film and fabric treatments. However, low-pressure plasma treatment is essentially a batch process with fabric being treated as it is wound from one batch to another inside a vacuum chamber.

There is a great need for commercially viable plasma systems able to perform continuous on-line treatment of fabrics and films for finishing and coating applications. For this purpose both the low-pressure and the atmospheric-pressure plasma systems would be suitable for processing of fibres, yarns and fabrics. Whereas some commercial low-pressure plasma systems have been around for a few years, lately there has been a push by some plasma machinery manufacturers to build atmospheric-pressure based plasma systems for on-line and in-line use and to market these for different types of functionalisation.

The industrial objectives for these plasma systems have been to produce plasma reactors and fabric-handling systems able to process continuous, roll-to-roll lengths of fabrics, process widths up to 5 metres or more, process at speeds of greater than 10 metres per minute, process at or near room temperature and obtain uniform, deep-penetration and surface modification of fibres in textiles and nonwovens, and be capable of handling large fabrics with wide electrode spacing.

Despite the proven capability and flexibility of plasma technology in the laboratory environment and despite very significant market potentials, the commercial use of the available plasma systems for industrial processing of textiles is still almost none. The systems offered in the European market are:

Low-pressure plasma systems capable of:
In-line treatment and batch treatment: Europlasma (Belgium), P2i (UK), Mascioni (Italy)

Atmospheric-pressure plasma systems capable of:
On-line treatment and batch treatment. On-line treatment and continuous systems: Dow Corning Plasma Systems (Ireland), Ahlbrandt (Germany), AcXys (France)

These companies offer standard and custom-designed machine construction as well as specially designed laboratory plasma units. Some companies have provided proprietary liquid precursor delivery/deposition systems. P2i has developed plasma chambers for treating end-products such as clothing.

Cost considerations

The cost of energy, chemicals and cooling water used in plasma treatments is relatively low. However, there is a big investment in machinery and personnel. The crucial factors for the customer company are expected utilisation rates and projected cycle times.

Plasma technology for textile finishing: Barriers and challenges

Although it has long been verified in laboratory and industrial plasma prototypes around the world that plasma technology is a versatile and environmentally friendly finishing process for achieving a broad spectrum of textile functionalisation, its application due to some known and unknown reasons has still not gathered commercial momentum. Some of these reasons may include important gaps in the relevant applied research, slow development of suitable industrial plasma systems, a late focus on developing on-line atmospheric pressure plasma systems and less public transparency regarding the successes and failures of industrial trials.

It is well known that all plasma machinery manufacturers do carry out interesting product development work for many textile and nonwoven companies. However, this work is mainly carried out under strict confidentiality agreements and consequently the successes and failures of these activities are not known in public. It is the editor's strong belief that the commercial application of plasma technology in the textile industry will gather momentum and will become widespread if there is more transparency as regards results and experience of textile companies that are successfully using this technology in their production.

About the book

The objective of this book is to give to the reader a comprehensive description of the science and technology related to plasmas, with particular emphasis on their potential use in the textile industry. The book contains, probably for the first time ever, a collection of the essential knowledge and information about plasmas as a smart engineering tool for obtaining the desired surface characteristics on fibres essential for producing high-functional and added value textiles, technical textiles and nonwoven products. The contributors to this book represent a team of international experts at the cutting edge of plasma technology and high-functional textiles.

In Chapter 1, Bill Graham gives a detailed description of the physics and chemistry of plasmas and describes how the unique physical and chemical characteristics of the plasma environment make it attractive for textile processing. The physical characteristics of plasmas are described in this chapter, along with the general chemical characteristics and surface interactions of partially ionised gases. The basic properties of the gases in which plasmas are formed, as well as the basic concepts of the creation of plasmas and their physical structure, are discussed along with the conditions that must prevail for an ionised gas to behave as plasma and the parameters that describe the plasma. The author then describes in detail the unique aspects of plasma chemistry with regard to the constituent species, their collisions and interactions. In textile processing, the interactions of the plasma generated species with and on the surfaces in contact with the plasma is of great importance and these are also discussed in this chapter.

In Chapter 2, James Bradley and Paul Bryant describe the diagnosis and control of plasma parameters in the processing of textiles and other materials. Plasma diagnostic tools are a useful, if not essential, element towards the proper understanding and development of technological plasmas. Knowledge of the particle densities and energies in the bulk and at boundaries, the electrical potentials in the system and the spatial and temporal evolution of all of these parameters allow physicists and technologists not only to operate plasmas in the most efficient way but also to allow the plasma intrinsic processes to be tailored to suit a particular process. The authors then describe various types of diagnostic tools that can be used depending on the type of plasma under investigation and the specific information that is required. The following four techniques are described in detail: (i) discharge electrical characteristics, i.e. the nature of the driving currents and voltages of a plasma discharge and their relationship, which can provide much information about the bulk plasma properties (interpretation of the driving current and voltage waveforms yields information on the major processes in the discharge); (ii) electric plasma diagnostics based on the electrical properties of plasmas, which are perhaps the most frequently used methods of determining the local plasma parameters such as electron density, N_{eo}, temperature, T_e, and plasma potential, V_p; (iii) plasma mass spectrometry, which is a well-developed technique that provides information on the identity of the neutral and charged species present in a discharge, and their relative fluxes to a material surface or substrate. The technique is also an ideal tool to understand the behaviour of plasmas with complicated mixtures of chemical precursors; (iv) optical emission spectroscopy. This section attempts to cover of the important aspects of optical emission spectroscopy and its use as a diagnostic. An exhaustive list of references has been included in this chapter.

In Chapter 3, Paul Lippens describes the low-pressure cold plasma technology for treatment of textiles and nonwovens. Description is given of the low-pressure vacuum plasma systems for plasma activation, plasma etching and plasma polymerisation of fabrics. The author then describes some existing equipment for low-pressure vacuum plasma technology including web treatment equipment based on box-type vacuum chambers as well as some roll-to-roll web treatment equipment. This is followed by presentation of results showing the benefits of vacuum plasma treatment on fabrics for automotive and medical applications, plasma pre-treatment prior to dyeing, activation of automotive textiles before application of flame retardant chemistry and hydrophobic nonwovens for filtration applications. The author mentions that, for most of these applications, industrial size low-pressure plasma machinery has already been manufactured and used. The author also discusses the economics of vacuum plasma treatment for fabrics and nonwovens.

In Chapter 4, Tony Herbert gives a comprehensive description of various types of atmospheric-pressure cold plasma processing technologies, including corona, dielectric barrier discharge (DBD) and glow discharge-based processes. He then describes in detail some of the most important basic manufacturability needs for industrially feasible applications of plasma technology. These include cool processing, large substrate area processing and high throughput. He states that the atmospheric pressure plasma (APP) type intrinsically capable of meeting the size and temperature constraints needed for textile processing is the atmospheric pressure glow discharge (APGD). He then describes, in detail, some existing APP equipments for textile processing. The APP equipment configurations for textile processing can be categorised according to the generic treatments that they can run and hence the kinds of surfaces that they can deliver. There are four main treatments: air treatment, controlled atmosphere treatment, gas precursor coating and liquid precursor coating.

According to Herbert, a key distinction between the different APP options is how they perform in relation to the critical ratio of added value/cost. Added value is strongly related to surface functionality or performance: the more sophisticated and powerful the properties of the treated surface, generally the higher its value. The author states that there is no 'superior' APP technology and that in the current state of development of plasmas for textile manufacturing there is no single ideal and clearly superior plasma technology for this. He adds that atmospheric-pressure plasma is not intrinsically superior to low-pressure plasma or *vice versa*.

In Chapter 5, Thomas Stegmaier, Alexander Rau, Albrecht Dinkelmann and Volkmar von Arnim describe atmospheric plasma systems with specific reference to the corona and DBD treatments of textiles for technical applications. The reasons why plasma processes at atmospheric pressure are advantageous for the textile industry are discussed, followed by a general introduction to the corona and DBD systems. The authors then describe some special adaptations of corona and DBD technology to textile processing, including the principles of the processes and equipment, mechanisms of surface activations involved, application of DBD treatment in some types of technical textiles and the stability of the effects after DBD treatments. Corona systems in combination with aerosols are described and examples are given of some hydrophobic and oleophobic treatments of textiles using the DBD type of plasma technique in combination with gas polymerisation and vaporised liquors.

In Chapter 6, Dirk Hegemann and Dawn Balazs have written about the nano-scale treatment of textiles using plasma technology. Plasma technology can be used for ablation and deposition processes. While ablation enables a complete cleaning of textiles from manufacturing residuals, deposition can be controlled in the nanometer range to achieve new functionalities. The textile properties remain unaffected by the treatments, both being dry and eco-friendly. Some advantages of plasma technology for the textile industry are described looking specifically at the advantages of nano-sized treatments as well as plasma methods with regard to the material types. The authors then examine the effectiveness of plasma cleaning, focusing on fabrics and fibres, as well as plasma metallisation and plasma polymerisation, investigating the special requirements for fabrics and fibres to achieve nano-scaled coatings, as well as the transfer to industrial-size processes (scale-up). Plasma co-polymerisation using a combination of sputtering and plasma polymerisation to obtain nano particles within a polymeric matrix is also described, and future trends are presented.

In Chapter 7, Stephen Coulson describes how plasma treatment can be used for producing water- and oil-repellancy, not only on textile fabrics but also on garments and other 3-dimensional textile products. This chapter considers the requirement for such repellency for textiles, and looks at the features and benefits, along with the critical factors, of a diverse number of products in a number of industry sectors. After describing the theory and testing of water- and oil-repellency and the current solutions for rendering textiles water- and oil-repellent, the author then describes the use of a new plasma system for imparting liquid repellency. This is covered by a case study of the scale-up issues faced with commercialising a low-pressure plasma process, and touches on some of the background work on the use of plasmas to achieve this technical effect. The chapter also covers the author's view on what the future holds in this field, and outlines a vision for plasma processing and important milestones that need to be achieved for the technology to be commercially acceptable.

In Chapter 8, Uwe Vohrer describes how to engineer biomedical textiles using plasma technology. The requirements of textiles (woven, nonwoven, knitted) for biomedical applications are manifold – minimised unspecific protein adsorption, biocompatibility (blood-, cyto-, or tissue-compatibility) or even active functionality (for coatings such as antibacterial finishing, bioactive layers or drug delivery systems) are some of of the demands on biomedical fabrics and scaffolds. After giving a brief introduction to the use of technical textiles for biomedical applications, as well as the plasma-based techniques, the author describes different methods for activation, functional grafting and polymerisation from the point of view of the interaction between plasma and biomedical textiles. One focus is on the introduction of specific functionalities by care for retention of the monomer structure. Some technical aspects of various experimental set-ups and industrial plants are described and some examples of the plasma finishing of biomedical textiles are given, including the assessment of the treated samples. In the final part of this chapter an outlook is given on the applications, products and markets, and future trends in this area are highlighted.

In Chapter 9, Helga Thomas describes plasma modification of wool, with particular reference to how wool-finishing plasma technology offers an enormous potential ranging from improved dyeing, printing and spinning performance to reduced felting tendency. Since concern for the environment and introduction of strict ecological legislation has caused an environmental pressure on the industry, the application of low-temperature plasmas to wool has recently regained increasing interest, particularly with a view to improvement of dye-uptake and replacement of the chlorination stages in commercial shrinkproofing and printing. This has resulted in a number of investigations about plasma-induced chemical and morphological changes in wool fibre. The observed differences in finishing and care performance of wool after plasma treatment are related to surface-specific changes of the protein fibre. The author then describes how the textile properties and the finishing performance such as dyeing, finishing, shrinkproofing and softening behaviour of wool fabrics are affected by plasma treatment. She concludes that the implementation of plasma technology into the wool industry is closely connected to further developments towards larger scaled machinery, allowing a cost-efficient treatment with special regards to a high material throughput, as well as to the development of highly effective tailored auxiliaries for achieving special effects.

In Chapter 10, Kenth Johansson describes how natural cellulose fibres can be modified by plasma treatment, for use both in fibrous products and in fibre composites. This chapter provides a general summary of the current state of knowledge of plasma modification of various natural cellulose fibres. However, an increasing awareness of the benefits and advantages of lingo-cellulosics, which are the most significant of renewable natural polymeric resources, has increased the interest in improving their properties further using plasma surface modification. After a brief presentation of various natural, regenerated and modified cellulosic fibres, the next section is devoted to exploring the mechanisms of interaction between them and various plasmas, including generation of free radicals and oxidation of cellulose surfaces using argon and oxygen plasmas. The author then describes how plasma modification of cotton fibre, which is the purest cellulosic fibre, results in improved surface properties in various textile applications and how plasma treatment on some ligno-cellulosic fibres (and also their thermoplastic counterpart) can improve the mechanical and adhesion properties of the resulting composite. Plasma surface modification of solid wood and wood pulp fibres is discussed, and the last section of this chapter deals with plasma modification of regenerated cellulose fibres such as Cellophane and viscose fibres.

In Chapter 11, Bruno Marcandalli and Claudia Riccardi describe the potential use of plasma treatment for finishing of fibres and textiles. Plasma treatments of textiles, especially in the last ten years, have been extensively studied. A very large number of papers have been published and patents registered on this subject, all focusing on different aspects of plasma processing, such as plasma generators and experimental set-ups, gas composition during plasma treatment, types of textiles treated and nature of modifications produced, plasma treatments for textile finishing, and product innovations. The authors go on to describe improvements in fabric properties after plasma treatment, such as enhancement of hydrophilic and hydrophobic properties, adhesion, dyeability and printability, antistatic and intelligent filter properties. They conclude by stating various advantages and problems associated today with the industrial plasma treatments for textiles.

Finally, in Chapter 12, Anne Neville, Robert Mather and John Wilson give descriptions of the characterisation of plasma-treated fabrics for assessing the change of a range of physical, chemical and topographical properties in their near-surface region. The techniques for surface analysis described are divided into two main categories – those that assess physical and topographical properties and those that assess chemical properties. The physical and topographical properties are measured by scanning electron microscopy (SEM) and atomic force microscopy (AMF) techniques and the chemical properties are measured using Fourier transform infrared (FTIR) technique. The authors also describe other techniques such as X-ray photoelectron spectroscopy (XPS) and the future possibilities of nanoindentation and X-ray absorption spectroscopy (XAS).

This book contains a collection of various scientific and technical aspects related to plasma technology, which has great potential as a feasible emerging processing technology for textiles and nonwovens. It is intended for readers representing various categories such as plasma researchers, polymer scientists, textile scientists and technical staff working at universities and research institutes; research and development (R&D) strategy and product-development staff of textile and nonwoven companies producing a range of different products; and undergraduate and graduate university students. The message that we get from the book is that plasma technology for textiles potentially offers a versatile, flexible and environmentally friendly finishing approach for imparting much desired functionalities in fibrous products.

Lately, many EU-financed projects within the 4th, 5th and 6th Framework programmes have had the objective of developing and demonstrating the feasibility of plasma-based industrial processes to meet the needs of the textile industry and offer tools for product development and innovation. According to the editor's experience, much of the reservation of the textile industry as regards adaptation of plasma technology is due to the lack of knowledge as well as uncertainty about this new and unfamiliar technology. This book is an attempt to help the textile industry overcome this barrier.

Additional information can be obtained in the following publications:

M. Sarmadi and Y. Kwon. Improved Water Repellency and Surface Dyeing of Polyester Fabrics by Plasma Treatment. *Textile Chemist and Colorist*, **25**: 33–40, 1993.

M. Rabe, K. Greifeneder, K. Truckenmuller, B. Petasch and E. Rauchle. Waterproofing and Improvement of the Dye Fastness of Polyester Yarn by Plasma Polymerization. *Melliand Textilberichte*, **75**: 513–517, 1994.

E. Godau, *Using Plasma Technology*, Textile Technology International, 1996.

R. Shishoo, Plasma Treatment – Industrial Applications and its Impact on the C&L Industry. *J. of Coated Fabrics*, **26**: 26–35, 1996.

R. Shishoo and S. Sigurdursen. Surface Properties of Polymers Treated with Tetrafluoromethane Plasma. *J. of Applied Polymer Science*, **66**: 1591–1601, 1997.

R. Shishoo. Atmospheric Pressure Plasma Treatment of Textiles and Nonwovens, *Proceedings of the IFAI Expo 1999*, 28–30 October 1999, San Diego, USA.

R. Shishoo. Proceedings of European Textile and Clothing Network – 'TERESA' meetings, published by EURATEX, Brussels; Public Conference, 28 April 1999, Public Conference 25–26 May 2000 & Research Strategy Workshop, May 8, 2001, Brussels.

R. Shishoo and J. Ohlsson. Use of Plasma Technology in Textile Processing – The Achievements and the Challenges Ahead, *Proceeding of the World Congress: High Performance Textiles*, July 4–5, 2001, Bolton, UK.

T. Oktem, H. Ayhan, N. Seventekin and E. Piskin. Modification of Polyester Fabrics by *in situ* Plasma or Post-plasma Polymerisation of Acrylic Acid, *Journal of the Society Dyers and Colourists*, **115**: 274–279, 1999.

K.H. Lehmann, D. Ganssauge and H. Thomas. Finishing of Fabrics – Influence of a Plasma Treatment on the Finishing Processes and the Fabric Properties. *International Wool Textile Organisation Congress.* 2001; 1–9.

Some relevant plasma projects within the EU's different framework programmes (source: CORDIS)

1. Endless fibre surface engineering by an industrially viable environmentally friendly plasma. Project Acronym: STAR, EU-programme BRITE/EURAM 3.
2. Development of plasma technology for continuous processing of textile fabrics and nonwovens. Project acronym: PLASMATEX, EU-programme BRITE/EURAM 3.
3. Continuous On-line Atmospheric Pressure Plasma Equipment based on dielectric barrier discharge technology for surface processing of various papers and textiles, fibres for composites and plastics. Project acronym: COLAPE. EU-programme GROWTH.
4. Development of high-performance fabrics based on industrial cold plasma technology. Project acronym: PLASMAFAB, EU-programme GROWTH.

5. Plasma technologies for textile, food, health and environment. Project acronym: PLASMATECH, EU-programme GROWTH.
6. Eco-efficient activation of hyper functional surfaces. Project acronym: ACTECO, EU-programme IP-SME.
7. Document TA3 ‘Atmospheric and low pressure plasmas’. Project acronym: LEAPFROG CA, EU-programme GROWTH.

Part I

Plasma science and technology

1

The physics and chemistry of plasmas for processing textiles and other materials

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1.1 Introduction

The unique physical and chemical characteristics of the plasma environment make it attractive for textile processing. A plasma is an ionised gas, i.e. it contains electrons, ions and neutral atoms and/or molecules. However, not all of the ionised gases used in textile processing will exhibit the properties associated with plasmas, mainly because of they have low charge state densities compared to the neutral gas density or are produced by transient phenomena. The physical characteristics of plasmas are described in this chapter, along with the general chemical characteristics and surface interactions of partially ionised gases. In Section 1.2 the basic properties of gases in which plasmas are created are introduced. Section 1.3 introduces the basic concepts of plasma creation and their physical structure, along with the conditions that must prevail for an ionised gas to behave as a plasma, and the parameters that describe the plasma. The unique aspects of plasma chemistry are described in Section 1.4 through discussions of the constituent species, their collisions and interactions. In textile processing, the interactions of the plasma generated species with and on the surfaces in contact with the plasma are of great importance and these are discussed in Sections 1.5 and 1.6, respectively.

1.2 Gases

The underlying neutral gas environment in the plasma systems used in textile processing can be quite complex and inevitably involves an initial mixture of atoms and molecules. The gas can be flowing and may have temperature and density gradients. However, the most useful approach to obtain a basic understanding of gas behaviour is through using kinetic theory. This approach makes the following assumptions: the gas consists of identical molecules; individual molecules are small compared to the average space between them; the molecules themselves are relatively incompressible; and the molecules are in constant random motion. So here the gas will be assumed to be single species, uniformly distributed and not flowing. In addition, for simplicity, the term molecule will be used to describe all the neutral particles unless otherwise stated.

The continuous motion of the molecules is quantified in terms of their temperature. The higher the temperature, then the more vigorous is their average motion. Molecules acquire or lose energy through collisions with one another or through contact with solid objects. This energy is in the form of kinetic energy (E_K), related to the mass (M) and velocity (v) of the molecule by the expression

$$E_K = \frac{1}{2}Mv^2 \qquad [1.1]$$

In a large population the molecules have a wide range of energies and the energy of an individual molecule is constantly changing. The energy distribution of such a collection of molecules is statistical and is described by a function known as a Maxwell–Boltzmann distribution The energy distribution can be defined by a single quantity, the temperature (T). The mean speed of molecules ($\bar{c}$) in such a gas is given by

$$\bar{c} = \sqrt{\frac{8kT}{\pi M}} \qquad [1.2]$$

where k is Boltzmann's constant = $1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$, T is in Kelvin and M is the mass of the molecule in kg. So, for example, nitrogen molecules in air at 20°C (293 K) have a mean speed of $500\,\mathrm{m\,s^{-1}}$.

In calculating the mean kinetic energy of the molecules in the gas, the mean square speed $\overline{c^2}$ is required, which for a Maxwell–Boltzmann distribution is given by

$$\overline{c^2} = \frac{3kT}{M} \qquad [1.3]$$

and therefore the average kinetic energy of the molecules is related to the gas temperature by the expression

$$\langle E_K \rangle = \frac{1}{2}M\overline{c^2} = \frac{3}{2}kT \qquad [1.4]$$

1.2.1 Mean free path

The moving molecules collide with one another. Between collisions, the molecules will travel in a straight line. Since the molecules are randomly distributed within the volume and are moving with different velocities, each one travels different straight line distances between collisions.

While $\bar{c}$ is the mean speed of the molecules, in collisions it is the relative mean velocity between molecules that is significant and this depends on the angle between the respective directions of motion of the molecules. It can be shown that for a Maxwell–Boltzmann velocity distribution and a uniformly dense gas, the mean velocity is $\sqrt{2}\bar{c}$.

If there are n_g gas molecules per unit volume, then the collision frequency (ν) or collision rate is given by

$$\nu = \sqrt{2} n_g \sigma_c \bar{c} \tag{1.5}$$

where σ_c is known as the cross-section for the collision between the molecules. The cross-section is the effective area that a molecule appears to have when approached by another molecule. The concept will be discussed in more detail in Section. 1.4.3. As the temperature increases, the particle velocity increases and so therefore does the collision frequency.

The collision mean free path (λ_c) in such a gas is therefore

$$\lambda_c = \frac{1}{\sqrt{2}\sigma_c n_g} \tag{1.6}$$

As the gas density increases, the mean distance a molecule moves between collisions decreases. The molecules in the air at atmospheric pressure and room temperature collide with each other with a frequency of about 10^9 collisions per second, with a mean free path between collisions of about 10^{-8} m. At 10 Pa, the mean free path increases to a few mm.

1.2.2 Particle flux and pressure

The particle flux (Γ) of a gas striking a unit surface or crossing an imaginary unit area from one side will depend on the velocity distribution of the gas molecules and the angular distribution of the molecular motion relative to the surface. Considering a static gas and molecules crossing the surface in a direction normal to the surface, it can be shown that

$$\Gamma = \frac{n_g \bar{c}}{4} \tag{1.7}$$

Then

$$\Gamma = n_g \left(\frac{k_B T}{2\pi M} \right)^{1/2} \tag{1.8}$$

i.e. the particle flux is directly proportional to the particle density and the square root of the gas temperature, and is inversely proportional to the square root of the mass of the molecules.

Pressure (P) is defined as the rate at which momentum is imparted to a unit area of surface. When a molecule bounces off a surface, there is a total change of momentum of $2M\bar{c}$ and so the rate of momentum change is $2M\overline{c^2}$. Molecules can be considered to be moving in six directions corresponding to the six faces of a unit cube, so on average $n/6$ molecules will cross a unit area in unit time. Therefore, from Equation 1.3

$$P = \frac{1}{3} M n_g \overline{c^2} = n_g kT \tag{1.9}$$

1.3 Plasmas

A gas is normally an electric insulator. However, when a sufficiently large voltage is applied across a gap containing a gas or gas mixture, it will breakdown and conduct electricity. The reason is that the electrically neutral atoms or molecules of the gas have been ionised, i.e. split into negatively charged electrons and positively charged ions. The nature of the breakdown and the voltage at which this occurs varies with the gas species, gas pressure, gas flow rate, the materials and the nature, geometry and separation of the surfaces across which the voltage is sustained, the separation distance of the electrodes, the nature of the high voltage supply (e.g. dc, ac, radiofrequency or microwave) and the actual electrical circuitry.

The resulting ionised gas is often called a discharge or plasma. Those used in textile processing vary considerably but are usually only partially ionised gases containing electrons, ions and neutral atoms and/or molecules. The interactions of the electrically charged particles with each other, with the neutral gas and with contact surfaces produce the unique physical and chemical properties of the plasma environment. This environment is distinct from that found in solids, liquids or gases; hence plasmas are sometimes called the fourth state of matter.

A plasma is defined as a collection of positive and negative charges which act collectively. This implies that not only do the charges exert coulomb forces on each other but also that these forces are as important as, and dominate over, externally applied forces and effects due to collisions between themselves and any neutral gas present. In other words, the 'self-generated' electric fields play an essential role in how the particles move. A major consequence of this collective behaviour is the ability of the plasma to screen out local density perturbations and to create a sheath region between the plasma and contact surfaces. Not all ionised gases or discharges can be classified as plasmas; certain criteria must be meet before an ionised gas will exhibit the phenomena associated with a plasma's collective behaviour.

1.3.1 Electron and ion temperatures

A similar approach to the kinetic theory of gases can be applied to the electrons and ions in an ionised gases with energy and momentum exchange through collisions, albeit more complex than in a gas. However, the momentum transfer between the light electrons and the heavier gas molecules and plasma ions is not very efficient and often the energy deposition into the plasma favours the electrons. As a result, ionised gases, particularly at low gas pressures and charged particle densities, are described as non-thermal. This means that the constituents, e.g. the electrons, ions and gas molecules are each in thermal equilibrium only with similar mass species. The velocity distribution of each species can be represented by a Maxwell–Boltzmann distribution and the energy distribution quantified by a temperature. However, often the electron temperature is very considerably higher than the ion and gas temperatures, i.e.

$$kT_e >> kT_i \approx kT_g$$

where T_e is the electron temperature, T_i is the ion temperature and T_g is the gas temperature. In low pressure (<100 Pa) plasmas, the gas and ion temperatures can be 300 K while the electron temperatures may be over 20 000 K. In the literature, the temperature and other energies are often presented in terms of electron volts (eV), where

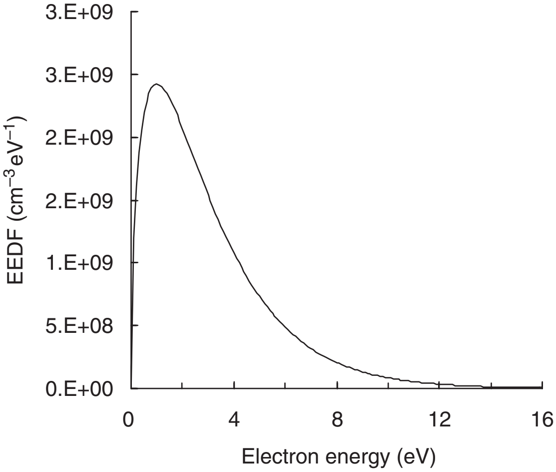
$$k\mathrm{T} = 1\,\mathrm{eV} \equiv 11\,600\,\mathrm{K}$$

The calculated Maxwell–Boltzmann energy distribution function for electrons with a density of $10^{16}\,\mathrm{m}^{-3}$ and temperature of 2 eV is shown in Fig. 1.1.

The mean speeds, mean free paths, collision frequencies and fluxes of electrons and ions can be calculated using the equations in Section 1.2 and the appropriate values for the electron and ion masses, temperatures and dominant collision cross-sections.

It is worth mentioning here that, in many low-pressure ionised gases, because of the electron heating mechanisms, inelastic collisions and the nature of the plasma, the electrons are not in thermal equilibrium and so their energy distribution is not represented by a Maxwell–Boltzmann distribution and cannot be defined by a temperature. This is discussed later.

As the electron-heavy particles collisions become more frequent, then the electrons transfer energy more rapidly and all the species approach the same temperature, so plasmas with high charged particle and gas densities are often described as thermal.



1.1 Calculated Maxwell–Boltzmann energy distribution function for an electron density of 10^{10} cm^{-3} at a temperature of 2 eV.

1.3.2 Quasineutrality

It is often stated that plasmas contain equal numbers of positively charged ions (n_i) and negatively charged electrons (n_e). The ionising events which maintain the plasma create an ion and electron pair and then the plasma self-sustains this charge equality. Consider a collection of these charges and then consider the removal of just one type, for example the electrons. Removing one electron leaves behind a net positive charge which will act to hold it back and removing more electrons results in a larger positive charge build up, making it increasingly harder to remove more electrons. So a great deal of energy is needed to separate the charges, and they consequently tend to stay together.

In fact, plasmas do not contain exactly equal numbers of electrons and ions, but the number of charges is huge and the difference is relatively small so we use the term quasi-neutrality and $n_e = n_i$ is a very good approximation.

1.3.3 Debye length

Plasmas act to screen out applied electric fields caused both by internal, localised inequalities in positive and negative charge densities and externally applied fields. Consider a quasi-neutral plasma and the introduction of a localised, enhanced electron density. The charge imbalance will generate a potential (ϕ), which will affect the surrounding ion and electron density. Since the electrons are much lighter than the ions, it can be assumed that the ions are static. The electrons' response to the potential will depend on their kinetic energy, which, if they are in thermal equilibrium, can be expressed in terms of the electron temperature. The electron density at the perturbation is given by

$$n_e = n_\infty \exp(e\phi/kT_e) \tag{1.10}$$

where n_∞ is the undisturbed density far away from the negative charge perturbation. In one dimension it can be shown that the plasma acts to shield out the potential created by the perturbation so that at a distance x away the potential is given by

$$\phi = -\phi_0 \exp(-x/\lambda_d) \tag{1.11}$$

where λ_d has the dimensions of length, is called the Debye length and it is given by

$$\lambda_d = \sqrt{\frac{\varepsilon_0 kT_e}{e^2 n_e}} \tag{1.12}$$

where ε_0 is the permittivity of free space.

If we compare this potential around a charge in a plasma to the potential around a single 'naked' charge in a gas or vacuum (which falls off as $1/x$), we see that it falls off much faster in the plasma. The physical meaning of this is can be qualitatively understand. The charges in a plasma are in constant motion, but since like charges repel and opposites attract, each charge collects around itself a 'cloud' of opposite charge which screens out its field at large distances. This screening effect eliminates any large electric fields from the plasma and so $n_e = n_i$. Another result is that the plasma is spatially uniform meaning that large-area ionised gas regions can be formed. If plasma conditions do not prevail, then local charge density fluctuations can be amplified.

A practical formula for calculating the Debye length is

$$\lambda_d \approx 7400\sqrt{\frac{kT_e}{n_e}} \quad \text{(m)} \tag{1.13}$$

where kT_e is in eV and n_e is in m^{-3}.

If Debye screening is to be effective, then the typical ionised gas dimension (L_p) must clearly be larger than the Debye length. So $L >> \lambda_d$ is a plasma requirement.

1.3.4 Plasma parameter

The screening effects associated with the discussion of the Debye length are based on a statistical description of the electrons. This is valid only for large numbers of particles. This can be expressed in the requirement that $N_D >> 1$, where N_D is the number of electrons contained in the Debye sphere, i.e.

$$N_D = n_e \frac{4}{3} \pi \lambda_d^3 \tag{1.14}$$

1.3.5 Plasma frequency

Any disturbance from quasi-neutral equilibrium will set up electric fields in a plasma. The electrons will move, in response to the fields, but as they accelerate they tend to overshoot the zero field position and oscillations are set up in the plasma. These oscillations occur at the plasma frequency (ω_{pe}) which can be written as

$$\omega_{pe} = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}} \tag{1.15}$$

where m_e is the electron mass. The plasma frequency is the natural 'ringing' frequency for the plasma. The electrons respond to an external disturbance on a time-scale given by the inverse of the plasma frequency.

A practical formula for the plasma frequency is

$$f_{pe} = \frac{\omega_{pe}}{2\pi} \approx 8.98\sqrt{n_e}\,(Hz) \tag{1.16}$$

where n_e is in m^{-3}.

While the lighter electrons dominate in the electric field screening, the ions also respond with a characteristic ion plasma frequency

$$\omega_{pi} = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_i}} \tag{1.17}$$

where m_i is the ion mass.

Collisions of electrons with gas molecules can damp these plasma oscillations, i.e. prevent them reacting with the time-scales required for collective behaviour. This requires that the electron collision frequency with molecules (ν_m) is less than the plasma frequency.

There are therefore three conditions for an ionised gas to behave as a plasma:

$$L_p >> \lambda_d \tag{1.18}$$

$$N_D >> 1 \tag{1.19}$$

$$\nu_m < \omega_{pc} \tag{1.20}$$

In a typical textile processing discharge, the electron densities are about $10^{16}\,\mathrm{m}^{-3}$ and the electron temperature is about 2 eV. From Equation 1.13, the Debye length is the order of 0.1 mm; from Equation 1.14, $N_D \sim 4 \times 10^4$ electrons; and from Equation 1.16, the plasma frequency is in the microwave region (GHz).

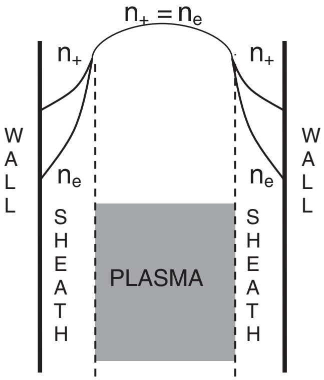
The electron collision frequency, calculated using appropriate values in Equation 1.5, is considerably lower than the plasma frequency at low gas pressures (<100 Pa) but at atmospheric pressure it is much higher than the plasma frequency and deviations from plasma behaviour might be expected under those conditions. In addition, if, as in for example microdischarges or streamers, the ionising events occur over time-scales close to that of the plasma period (10^{-9} s), then again plasma behaviour is not expected and local charge density fluctuations can be amplified. These and other small dimension ionised gases might also not comply with the requirement that $L_p >> \lambda_d$.

1.3.6 Plasma structure and the sheath

In any textile processing application, the ionised gas will come into contact with a solid object. As well as the textile material, metal or dielectric-covered electrodes and chamber walls may be in contact with the plasma. If the ionised gas meets the criteria discussed above and can be characterised as a plasma, then potential structures will be created.

Initially, both electrons and ions move to the solid surface. The ion and electron fluxes can be determined from an equation similar to Equation 1.8. In the steady state, to maintain quasi neutrality, the ion and electron fluxes must of course be equal, but since the electron velocities are greater than the ion velocities and since their densities are equal, the electron flux at the plasma edge is greater than that of the ions. The plasma therefore self-adjusts to balance the loss rate of the ions and electrons. The positive charge left behind after the initial loss of electrons concentrates near the solid in a thin layer called the plasma sheath. This region is usually quite thin, is not quasi-neutral and so has potential gradients. These act to reflect electrons back into the plasma and accelerate the ions to the wall, creating a flux balance, so that in the plasma $n_i = n_e$ but in the sheath $n_i > n_e$. In many plasmas, the sheath can be seen as a thin, dark layer between a luminous region in the plasma and the contact surface. It is especially easy to see near electrodes that are driven with large voltages.

A result of the sheath creation and its associated electric fields is that the plasma is at a positive potential relative to any contact surfaces. This is known as the plasma potential. The magnitude of the plasma potential depends on a number of different parameters but clearly the ratios of the ion to electron masses and temperatures play a significant role. Similar



1.2 Plasma densities in a plasma and its sheaths.

arguments to those given above show that an electrically isolated object in the plasma will attain a negative potential relative to the plasma so as to balance the ion and electron flux. This is known as the floating potential.

The structure of a contained plasma is illustrated in Fig. 1.2. The quasi-neutral plasma is field free and sits at a positive potential relative to the grounded contact surfaces. Between the surface and the plasma is the sheath, a non-charge neutral region in which there is an electric field sustained by the potential gradient. This means that ions are accelerated towards the surface and therefore arrive with a kinetic energy determined by the plasma potential. This kinetic energy can be increased by biasing the contact surface so, depending on the operating conditions, ions with a well-defined energy, ranging from a few eV to keV, can be incident on the contact surface. In addition, any electrons produced at the surface or in the sheath region will be accelerated back into the plasma. This can be an efficient way of coupling energy into the plasma.

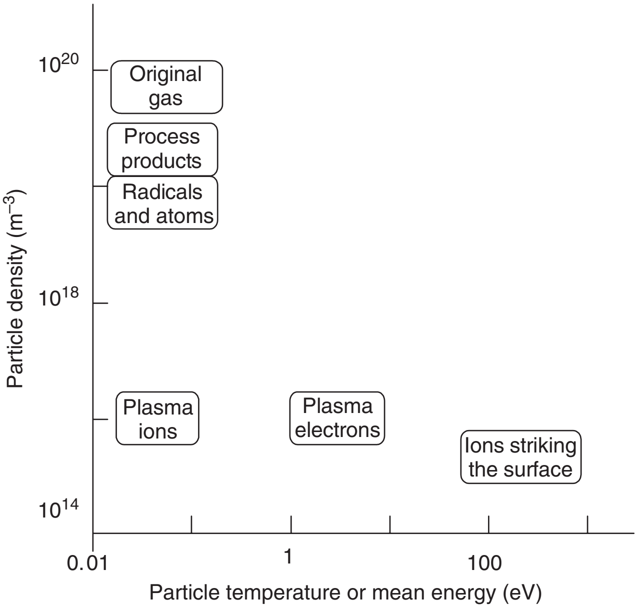
1.4 Plasma chemistry

1.4.1 Constituent species

Most processing plasmas are created in a molecular gas or a gas mixture that contains molecules. There are therefore a very large number of constituent species. The energy required to remove a single electron from a molecule or atom is known as the ionisation potential. The energies required to break molecules into various constituent parts are called the dissociation energies. As shown in Table 1.1, these are generally lower than the ionisation potential of the molecule and so there is often a high degree of dissociation in ionised gases. Dissociation products of the initial molecules are particularly important since they can be chemically reactive with the contact

Table 1.1 Energies characteristic of some atoms and molecules

Atom or molecule	Ionisation potential (eV)	Electron affinity (eV)	Metastable energy level (eV)	Lowest excitation energy (eV)	Dissociation energy (eV)
H	13.6	0.75		10.2	
He	24.6		19.8	21.2	
O	13.6	1.5	1.97	9.2	
F	17.4	3.5		12.7	
Cl	13.0	3.6		8.9	
H_2	15.6			11.5	4.5
O_2	12.5	0.45	1.2	7.9	5.1
Cl_2	13.2	2.5			2.5
C_6H_6	9.6				



1.3 Densities and temperatures or energies for the constituent species in a typical low pressure plasma.

surfaces. In Fig. 1.3, the approximate densities and temperatures or energies of the plasma constituents in a typical low-pressure plasma are shown. Some atoms and molecules can accommodate an extra electron, so creating negative ions; the stability of such negative ions can be gauged from their electron affinity and some values for these are shown in Table 1.1.

In addition, the electronic structure of the constituent atoms and molecules may be temporarily excited from its lowest (ground state) configuration to a higher energy, excited state level, usually in a collision with an electron. The additional energy is then released by the emission of light, generally in tens of nanoseconds or less, as the atom or molecule returns to its ground state. This light emission ranges from the infrared red to the vacuum ultra violet and can also produce chemical changes on the contact surfaces. However, sometimes the atomic or molecular excited state has an electronic structure that delays the light emission for up to a few seconds. These are called metastable states and they can play an important role in plasma initiation and plasma chemistry.

The constituent atoms of the molecules are not at rest but are in constant motion, both rotating around a common centre of mass and vibrating along their common axes. This rotational and vibrational motion has a lowest energy state; energy transferred to the molecule in collisions can increase the level of rotational and vibrational excitation of the molecule. The energy level differences are typically only about 0.001 to 0.01 eV for rotational states and 0.1 to 0.4 eV for vibrational states. The behaviour of the molecule in a collision can be influenced by its level of rotational and vibrational excitation since high ro-vibrational states can be excited with total energies of up to several eV.

1.4.2 Collisions

Just as in a neutral gas, as discussed in Section 1.2, the moving charged and neutral particles are colliding or interacting and reacting. The presence of energetic charged particles, particularly the electrons, lead to unique plasma chemistry. There are a huge number of interactions that can take place, particularly in a molecular plasma. In each collision, momentum and energy must be conserved. The collisions can be broadly classified into three types:

(i) Elastic collisions in which the momentum is redistributed between the colliding particles; the incident particles change direction but their total kinetic energy remains unchanged.
(ii) Inelastic collisions in which the momentum is redistributed between the colliding particles but where some fraction of the initial kinetic energy is transferred to the internal energy of one of the participating particles. This leads to the dissociation, excitation or ionisation of one or both of the participants.
(iii) Superelastic collisions in which the momentum is redistributed between the colliding particles and where the internal energy from one or both of the participants is transferred to the final total kinetic energy of the participants.

Table 1.2 lists some of the important types of reactions that occur in plasmas where most of the collisions involve only two particles. At higher pressures, collisions involving three bodies become probable. This allows even more diversity of reactions since the third body takes away momentum and allows reactions not physically possible between the other two bodies to occur. The third body can be another atom, molecule, electron or a surface. In some apparent two-body collisions, an emitted photon can take on the role of a third body.

As mentioned previously, some atomic or molecular states may be long-lived. These metastable states usually make a collision before they radiate, transferring their electronic energy to another constituent of the plasma. This energy may be enough to ionise a neutral atom or molecule with a lower ionisation potential in the collision. This is called Penning ionisation. Inert gases have particularly high energy, long-lived metastable states. The

Table 1.2 Some of the possible reactions of plasma constituents in the plasma volume

Reaction type	Name	
Electron impact	Ionisation	$e + A \rightarrow 2e + A^{+}$
	Dissociation	$e + AB \rightarrow e + A + B$
	Dissociative ionisation	$e + AB \rightarrow 2e + A + B^{+}$
	Dissociative attachment	$e + AB \rightarrow A^{-} + B$
	Electronic excitation	$e + A \rightarrow e + A^{*}$
	Ro-vibrational excitation	$e + AB \rightarrow e + AB\ (v, j \geq 1)$
	Momentum transfer	$e + A \rightarrow e + A$
Neutral	Dissociation	$AB + M \rightarrow A + B + M$
	Penning Ionisation	$A\mathit{m} + B \rightarrow A + B^{+} + e$
	Atom transfer	$A + BC \rightarrow AB + C$
	Rearrangement	$AB + CD \rightarrow AC + BD$
	Recombination	$A + B + M \rightarrow AB + M$
	Energy transfer	$A^{*} + B \rightarrow A + B^{*}$
	Relaxation	$A^{*} + B \rightarrow A + B$
	Momentum transfer	$A + B \rightarrow A + B$
Ion	Neutralisation	$A^{-} + B^{+} \rightarrow A + B$
		$A^{-} + BC^{+} \rightarrow AB + C$
	Associative detachment	$A^{-} + B \rightarrow AB + e$
	Charge transfer	$A^{+} + B \rightarrow A + B^{+}$
		$A^{-} + B \rightarrow A + B^{-}$
	Dissociative charge transfer	$A^{+} + BC \rightarrow A + B + C^{+}$
	Momentum transfer	$A^{+} + B \rightarrow A^{+} + B$

Note that e represents electron, * an electronically excited state, v and j the vibrational and rotational quantum numbers, respectively, A*m* a long-lived metastable state and M indicates any molecule and indicates third-body stabilisation.

metastable states represent a storage of energy within the atoms or molecules and they can play an important role in the kinetic behaviour of plasmas. Vibrationally and rotationally excited states often have long lifetimes, and although the total energies involved are generally less than for atom metastable states, they can also act as an energy reservoir in the plasma and can, for example, influence the electron temperature through superelastic collisions.

1.4.3 Cross-sections and reaction rates

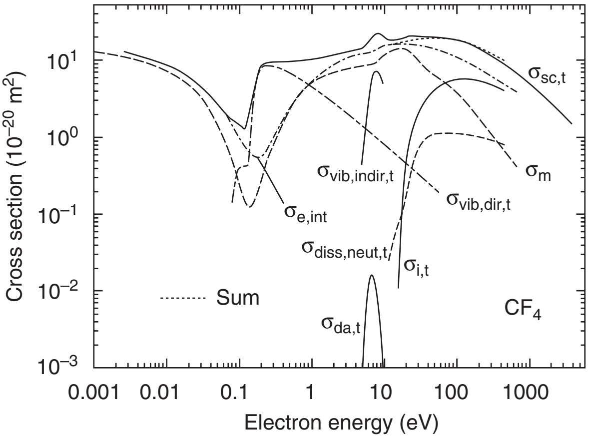
Collision cross-sections (σ_c) quantify the probability of a collision taking place between two or more particles. For two bodies in collision this represents the effective area of a particle as seen by another passing particle. This is unique to any pair of particles; for example, the interaction between two charged particles will be stronger than that for two uncharged particles and so the cross-section will be larger. The strength of the interaction between the two particles will also depend on the length of time for which they interact, i.e. their relative velocity or energy. There may also be threshold energy for a reaction to be possible, e.g. from Table 1.1, for the ionisation of a molecule (O_2) by an electron, the kinetic energy in the collision must at least be equal to the ionisation potential of the molecule (12.5 eV). Information about cross-sections for the many diverse reactions in a plasma is essential for an accurate insight into the plasma chemistry. Unfortunately, in many cases the data are sparse. However, the pervasive use of fluorocarbon plasmas in the microelectronics industry means that there are some quite comprehensive databases. Figure 1.4 shows some of the energy dependences of cross-sections for a wide range of collision processes in CF_4 but which are typical of the type of collisions in molecular plasmas.

1.4.4 Reaction rates

The number of collisions between two particle species (*1* and *2*) per unit time per unit volume (R_{12}) depends on the number density of both species, the cross-section and the time taken for the particles to move from one potential collision to the other, which in turn depends on their relative velocity (v), i.e.

$$R_{12} = n_1 \, n_2 \, \sigma_c(v)v \qquad [1.21]$$

As discussed earlier, in a plasma, the particles have a distribution of velocities, more often expressed as their energy distribution. The plasma chemistry pathways are frequently initiated by electron collisions. Equation 1.21 is therefore often written as



1.4 Energy dependence of cross-sections for electron collisions with CF_4. The notation refers to inelastic collisions (e,int), vibrational excitation (vib), dissociation of neutral molecules (diss,neut), inelastic dissociative attachment (da) etc. t refers to theoretical calculations. (from Christophorou, L.G. and Olthoff, J.K. (2002), *Applied Surface Science*, 192, (1–4), 309–326).

$$R_{12} = n_1\, n_2 <\sigma_c(\nu)\nu> \qquad [1.22]$$

where $<\sigma_c(\nu)\nu>$ is a mean value over the velocity distribution for a given temperature, is often written as K the rate constant and has units of area times velocity, e.g. m^3s^{-1}. These rate constants have different functional dependences on temperature because of the different energy dependences of the collision cross-sections, as illustrated in Fig. 1.4.

1.5 Plasma–surface collisions

The collisions of the plasma constituent species with the contact surface are the most significant interaction in materials processing applications. The plasma can deliver *kinetic energy* through ions accelerated in the sheaths and by vibrationally excited molecules, *potential energy* through the charged ions and metastable states, *chemical energy* through plasma-produced reactive atoms and radicals and *electromagnetic energy* (light) from the decay of electronically excited species. The interaction with the surfaces is complex and many different processes can occur; a few important ones are listed in Table 1.3. Since there has been no detailed studies of specific plasma–textile surface interactions, the following discussion will mainly focus on defining the various interactions which have been studied for solid surfaces and which may affect exposed textile surfaces.

Table 1.3 Some of the collisions and reactions of the plasma constituents with a surface

Reaction type	Name	Reaction
Neutral	Adsorption	$A + (s) \rightarrow A(s)$
	Desorption	$A(s) \rightarrow A + (s)$
	Dissociative adsorption	$AB + (s) \rightarrow A(s) + B(s)$
	Associative desorption	$A(s) + B(s) \rightarrow AB + (s)$
	Reaction at surface	$A + B(s) \rightarrow AB(s)$
	Reaction on surface	$A(s) + B(s) \rightarrow AB(s) + (s)$
	Electron emission	$A_m + (s) \rightarrow A(s) + e$
Ion	Neutralisation	$A^+ + e(s) \rightarrow A + (s)$
	Sputtering	$A^+ + e + B(b) \rightarrow A + B$
	Assisted desorption	$A^+ + e + B(s) \rightarrow A + B + (s)$
	Enhanced etching	$A^+ + e + B(s) + C(b) \rightarrow A + BC + (s)$
	Incorporation into bulk	$A^+ + e \rightarrow A(b)$
	Electron emission	$A^+ + (s) \rightarrow A(s) + e$

Note that e represents an electron, (s) an open surface site, A(s) a species A bound to the surface, B(b) a B species in the bulk and A*m* a long-lived metastable state.

1.5.1 Ion impact

At low ion energies, <15 eV, the ions lose energy and exchange momentum with the outermost atomic layers. Here, the potential energy of the ion, through its ionisation potential, plays an important role and at metal and semiconductor surfaces. The incoming ions can also be entrapped inside the solid if their kinetic energy is entirely dissipated in collisions with the atoms of the solid. As the energy increases, the penetration depth increases and so too does the entrapment. This can be strongly influenced by the porosity of the surface, with channels, etc. enhancing the trapping.

Ions striking a surface with energies above about 15 eV can remove atoms from the surface. This process is known as sputtering and it plays a key role in many plasma deposition and etching processes. Sputtering results from the transfer of kinetic energy and momentum from the incident ion to the atoms in the solid. If enough momentum is transferred to an atom in the direction of the surface, so that it has sufficient kinetic energy to overcome its surface binding energy, then that atom will be liberated (sputtered) from the surface. The number of particles sputtered per incident particle is very sensitive to the ion energy, the ratio of the masses of the incident and target particles, and the properties of the solid and surfaces. For metals, at around 30 eV only one atom is sputtered for every one thousand incident ions, but this increases to one atom for each incident ion at about 1 keV.

Atoms interacting with surfaces at these energies behave in a similar way to ions, since the ions are neutralised as they approach the surface. Relatively small neutral and ionic molecules (<6 atoms) approaching the surface will exhibit similar behaviour to atoms and atomic ions at the same energy. However, each atom can appear to interact separately and locally with the surface and with a total kinetic energy that is the ratio of its mass relative to the number of constituent atoms of the molecule. This means that molecules generally require higher energies than atoms and atomic ions to produce the same effect. Large molecules will dissipate their energy over very many surface atoms and their energy can usually be accommodated within the lattice of the solid and so have little effect. Molecules also bring energy to the surface in the form of their rotational and vibrational excitation.

As well as the reflection and sputtering of incident atoms and ions, particle impact can also produce electrons, particularly at metal electrode surfaces. These are accelerated into the plasma by the sheath potential and so they can play a very important role in sustaining the plasma. There are a number of different processes that can lead to electron production. On metals, if the ionisation energy of the atom of an incident ion is twice the work function of the surface, then an electron can be emitted by a process called potential emission, but this is not significant on insulating surfaces. There is also kinetic emission of electrons from solids resulting from the ionisation of the atoms in the solid by the transfer of energy from the rapidly moving incoming ions or atoms. If an electron is produced with sufficient energy, it can escape through the solid to and beyond the surface. This therefore requires comparatively high-energy incoming particles and the threshold ion energies for metals are generally around 1 to 2 keV. The yield around threshold is less than about 0.05 electrons per incident particle. However, kinetic electron emission yields from insulating and semiconductors are generally higher than those from metals and the thresholds energies are a few hundred electron volts. The photoelectric emission of electrons as a result of plasma light emission is often ignored but it is thought to play a significant role in the development of some high-pressure arcs and microdischarges.

1.5.2 Atom and molecule reactions

The atoms, molecules and radicals will arrive at the surface with a thermal distribution of energy which in most textile processing plasmas will be just above room temperature. They react both with and on the surfaces.

Absorption

Atoms, molecules and radicals can be adsorbed due to an attractive force between an incoming molecule and a surface. If it is Van der Waals force, produced by an electrostatic attraction caused by a mutual polarisation of two interacting atoms, then this is known as physisorption. This is a weak interaction with the bond energies between about 0.01 and 0.25 eV.

If a chemical bond is formed, i.e. there is a sharing of valence electrons by the interacting atoms, this is known as chemisorption and the energies are those associated with chemical bonds, i.e. from about 0.4 to 4 eV.

The incoming atoms and molecules that stick to the surface are termed adsorbates. If A is the incoming atom and S is the surface, both adsorption phenomena can be represented by the following reaction

$$A + S \rightarrow A{:}S \qquad [1.23]$$

An incoming molecule ($A{=}B$) with multiple (double, triple, etc.) bonds can be chemisorbed by the breaking of one of its bonds, e.g.

$$A{=}B + S \rightarrow AB{:}S \qquad [1.24]$$

while single-bonded molecules are often dissociated as they are bound to the surface

$$AB + S \rightarrow A{:}S + B{:}S \qquad [1.25]$$

This requires that there are two sites available on the surface and is known as dissociative chemisorption.

Not all atoms or molecules incident on the surface are adsorbed. The sticking coefficient (s) is defined as the flux of molecules that are adsorbed (Γ_{ads}), over the flux of molecules incident onto the surface (Γ_A), and from Equation 1.7

$$\Gamma_{ads} = s\Gamma_A = \frac{1}{4} s n_{AS} \bar{c}_A \qquad [1.26]$$

where n_{AS} is the gas density close to the surface and $\bar{c}_A$ is the mean atom or molecule speed.

In general, s depends on the relative reactivity of the incident atom or molecule with the surface, the gas temperature and the fraction of the possible sites on the surface that the incident atom or molecule can occupy. Generally, chemisorption only occurs until all the available sites on the surface are occupied, i.e. there is a monolayer of adsorbate molecules or atoms on the surface. Further absorption is by the much weaker physisorption.

Desorption

Desorption is the reverse reaction to adsorption and so can be written as the reaction

$$A{:}S \rightarrow A + S \qquad [1.27]$$

In thermal equilibrium, adsorption and desorption are in balance. Associative desorption is the reverse of dissociative adsorption.

$$2A{:}S \rightarrow A_2 + 2S$$

or $$A{:}S + B{:}S \rightarrow AB + S \qquad [1.28]$$

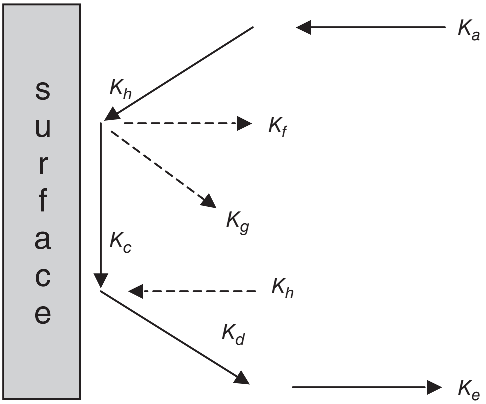
1.5.3 Surface kinetics

As with plasma chemistry, the relative probability that particular processes will happen can be described in terms of rate constants (K). Figure 1.5 considers a plasma in contact with a surface with which it can react chemically; the reactive atoms or molecules flow from the plasma, arriving at the surface at a rate (K_a), where they are adsorbed (K_b) and react chemically (K_c) to produce some product, which then desorbs (K_d) and flows into the gas phase (K_e). Alternatively, the reactive atoms may desorb without undergoing any reaction (K_f) or may undergo associative desorption with a reactive atom already on the surface (K_g). Finally the reaction products in the gas phase can return to the surface (K_h).

Consider the reaction of an atom A with a surface S. It can be adsorbed and subsequently desorbed.

$$A + S \underset{K_d}{\overset{K_a}{\leftrightarrow}} A{:}S \qquad [1.29]$$

If n'_0 is the area density (m^{-2}) of available adsorption sites for A on the surface S and $n'_{A:S} = n'_0\theta$ is the area density of sites covered with adsorbed molecules (m^{-2}s^{-1}). (Note: $'$ is used to indicate an area density rather than a volume density.) Then the flux of A adsorbing onto the surface is



1.5 Schematic of the processes that can occur when a reactive species interacts with a surface.

proportional to the fraction of sites not covered with adsorbate, i.e. $1 - \theta$, so the flux of atoms adsorbing to the surface is

$$\Gamma_{ads} = K_a n_{as} n'_0 (1 - \theta) \qquad [1.30]$$

where K_a is a second order rate coefficient.

In equilibrium this will equal the flux of atoms desorbing from the surface

$$\Gamma_{desorb} = K_d n'_0 \theta \qquad [1.31]$$

where K_d is a first-order rate coefficient.

$$\theta = \frac{\frac{K_a}{K_d} n_{as}}{1 + \frac{K_a}{K_d} n_{as}} \qquad [1.32]$$

i.e. if the adsorption and desorption rates and the gas atom density are known, the coverage of atoms on the surface can be calculated.

1.5.4 Plasma chemistry: Some unique features

The simple analysis presented above ignores the complexity of the plasma environment, where there are many different atomic and molecular, and neutral and charged, species incident on the surface. The microelectronics industry has used plasma phenomena with great effect, e.g. to obtain material selectivity and complex etch profiles. While the processes developed there may not be directly applicable to textile processing, some of the concepts and techniques might well find application. Examples are the use of gas mixtures to control surface reactions, balancing deposition and etching rates, and using the physical sputtering by the sheath accelerated ions, synergistically with surface chemical reactions.

1.6 Summary

There is an increasingly wide variety of approaches to generating ionised gases for textile processing. The primary motivation is to be able to generate specific reactive species from relatively inert feedstock gases. In ionised gases, and particularly in plasmas, these reactive species can be produced by energetic electron collisions with molecular precursors. Since the momentum transfer between the light electrons and the heavier gas molecules and plasma ions is not very efficient, as a result in plasmas, this highly reactive chemistry can be created in an environment where the ion and gas temperatures remain close to room temperature particularly at low gas pressures and charged particle densities.

A plasma is defined as a collection of positive and negative charges which act collectively. This implies that not only do the charges exert coulomb forces on each other, but also that these forces are dominant over, externally applied forces and effects due to collisions between themselves and any neutral gas present. A major consequence of collective behaviour is the ability of the plasma to screen out local density perturbations and to create a sheath region between the plasma and contact surfaces. Ions which diffuse through the plasma to the sheath edge are accelerated towards the surface. This delivers additional kinetic energy to the surface, along with the flux of reactive species, and can be used for process selectivity.

However, not all ionised gases or discharges can be classified as plasmas. Certain criteria must be meet before an ionised gas will exhibit the phenomena associated with plasma collective behaviour.

The criteria used in defining a plasma have been presented, along with the potential structure of the plasma and the electron-collision dominated plasma chemistry. The interaction of the plasma-created species with the contact surfaces has been described.

There is much unknown about the underpinning plasma physics and chemistry aspects of textile processing. The dominant role that plasmas have held in the microelectronics industry has driven much of the research to date and most of our basic ideas on low-pressure plasma processing of textiles derives from that work, but it may be inappropriate. Sheath formation near textile materials' surfaces has still to be explored. Also the required chemistry is very different and often more subtle, so for example the effect of charged particle bombardment and plasma light emission on the textile surface chemistry has yet to be resolved. The underpinning plasma and surface chemistry of the precursor gases of interest is still in its early stages.

There is a huge interest in using atmospheric-pressure ionised gases in textile processing. Here, the ionised gas may not be a plasma; however, there may be important exceptions, e.g. atmospheric-pressure glow discharges. There is still much to be done to understand the physics and chemistry in this revitalised area of high-pressure, non-thermal ionised gases.

1.7 Bibliography

Glow Discharge Processing, B. Chapman (John Wiley & Sons) 1980. This is a very good beginning level entry point for scientists and engineers interested in the field of low-pressure ionised gases, sources and surface interactions. It is focused largely on aspects of interest to the microelectronics industry.

Principles of Plasma Discharges and Materials Processing (Second Edition), M.A. Lieberman and A. Lichtenberg (John Wiley & Sons) 2005. This book provides a

very comprehensive and technically detailed account of the underlying science of low-pressure plasma processing, again orientated to the interests of the microelectronics industry.

Industrial Plasma Engineering (Volumes 1 & 2), J.R. Roth (Institute of Physics Publishing) 1995 and 1997. These two ambitious volumes cover the complete spectrum of industrial plasma science and technology from fundamental plasma physics to the engineering details of plasma sources at both low and high pressure.

Non-equilibrium Air Plasmas at Atmospheric Pressure, Editors: K.H. Becker, U. Kogelschatz, K.H. Schoenbach and R.J. Barker (Institute of Physics Publishing) 2005. This is a very comprehensive, detailed review of high-pressure non-equilibrium plasmas covering both the underlying science and technology.

2

The diagnosis of plasmas used in the processing of textiles and other materials

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2.1 Introduction

Plasma diagnostic tools are an essential element towards the proper understanding and development of technological plasmas. Knowledge of the particle densities and energies in the bulk and at boundaries, the electrical potentials and the spatial and temporal evolution of these parameters allow technologists to operate plasmas in the most efficient way and allow the intrinsic plasma processes to be tailored to suit a particular application.

There are many different diagnostic tools that can be used, depending on the type of plasma under investigation and the specific information that is required. Here, we have chosen to highlight four techniques frequently used in both academia and industrial settings. The first of these is the interpretation of the driving current and voltage waveforms. These measurements do not affect the plasma and can yield useful information on the major processes in the discharge. The second is electrical probing which, by their nature, are intrusive, since their presence affects the plasma under investigation. Their use is usually confined to low-pressure and low-temperature plasmas in which the heat flux will not destroy the integrity of the probe. The third area is mass spectrometry, which is most often performed at the substrate or plasma boundaries and may in many cases not affect the plasma unduly. The fourth diagnostic method discussed, optical emission spectroscopy, is non-perturbing; however, interpretation of spectral response is often difficult in low-pressure plasmas where the species are not in local thermodynamic equilibrium.

The field of plasma diagnostics is a large and varied one, and here we wish only to present the basics, applicable to the type of discharges used in the treatment of textiles, allowing readers to find more detailed and specific information relevant to their applications.

We recommend the following texts, which concentrate on or have included within, excellent sections on plasma diagnostics: Hutchinson (1994), Hippler *et al.* (2000), Biederman (2004), Becker *et al.* (2005) and Ovsyannikov and Zhukov (2000).

2.2 Discharge electrical characteristics

The nature of the driving currents and voltages of a plasma discharge and their relationship can provide a lot of information about the bulk plasma properties, these being the physical and chemical plasma processes, the effective plasma impedance, the power absorbed in the plasma, the discharge efficiency and mode of operation. In general, the current–voltage relationship will be a complex function of the external parameters (e.g. geometry and method of plasma excitation), and will affect the intrinsic plasma parameters (e.g. potential, plasma density and temperature). This relationship is given essentially by the effective series impedance of the bulk plasma and the boundary sheaths that connect the plasma to the walls and electrodes. This impedance may be complex (i.e. have a reactive component) or, in some cases, may be mainly resistive. The latter is particularly relevant for d.c. plasmas. The type of measurements that can be made of the excitation voltage and current depends on the method of excitation of the plasma itself. For instance, measuring d.c. voltages and currents is a very different task from mid-frequency a.c. waveforms and those at RF frequencies. For discharges sustained by electrical means we believe all good diagnostic work on a plasma should start with determining the relationship between the discharge current and voltage.

2.2.1 Simple model of the d.c. plasma impedance

In plasmas produced by electrical means, the electrons (initially produced by cosmic radiation) are accelerated by the application of electric fields and transfer their energy to the neutrals by ionising collisions. This is a necessary process for sustaining the discharge. Ions and electrons lost by diffusion to the walls and recombination processes (three-body and radiative) must be replaced by electron impact ionisation of neutrals. The electrons, which have a much higher mobility than the ions, will absorb the largest amount of power from the driving electric fields and carry most of the discharge current.

For electrons in a weakly ionised plasma (dominated by electron–neutral collisions) the electrical conductivity is $\sigma = eN_{\mathrm{eo}}\mu_{\mathrm{e}} = e^2N_{\mathrm{eo}}/M_{\mathrm{e}}\nu_{\mathrm{m}}$ (Lieberman and Lichtenberg, 1994). Here μ_{e} is the mobility, N_{eo} is the bulk electron density, M_{e} is the electron mass, e is the electronic charge and ν_{m} is the electron–neutral collision frequency. The conductivity then increases linearly with electron density and decreases with collision frequency; the latter is dependent on the density of the neutral particles (i.e. the neutral pressure). Thus, we can see that the current density j (= σE where E is the electric field) in such a discharge is proportional to the plasma density N_{eo}.

For a typical weakly ionised argon plasma with $N_{eo} \sim 10^{16}\,\mathrm{m}^{-3}$, electron temperature $T_e \approx 3\,\mathrm{eV}$ (thermal speed $v_{th} \sim 10^6\,\mathrm{ms}^{-1}$) and a pressure of $\approx 0.3\,\mathrm{Pa}$ (mean-free-path $\lambda_{en} \approx 0.5\,\mathrm{m}$), we have $\nu_m = v_{th}/\lambda_{en} \approx 2 \times 10^6\,\mathrm{s}^{-1}$ and $\sigma \approx 78\,\Omega^{-1}\,\mathrm{m}^{-1}$. This means, for a plasma column of cross-sectional area A of, for example, $2.5 \times 10^{-3}\,\mathrm{m}^2$ and length L (cathode–anode separation) of 0.1 m, the bulk plasma resistance would be $R_p = L/A\sigma \approx 0.5\,\Omega$.

However, in the sheath regions at the cathode and anode, the electron concentration is small (negligible in most cases) and the d.c. sheath impedance, R_s, is much larger. We can approximate the sheath impedance to be $R_s \approx V_s/I_B \approx (V_p - V_c)/AeN_{io}C_B$ where A is the effective cathode area, $C_B = (eT_e/M_i)^{1/2}$ the ion acoustic (Bohm) speed, V_p the plasma potential M_i is the ion mass, and V_c the cathode potential. For $A \approx 3 \times 10^{-3}\,\mathrm{m}^2$, $N_{io} \approx N_{eo}$ (quasi-neutrality approximation), $V_p - V_c \approx 100\,\mathrm{V}$ and, given the plasma parameters stated above, this would give a sheath resistance of $R_s \approx 7.75\,\mathrm{k}\Omega$. The sheath has greater impedance than the bulk plasma and in many low-pressure d.c. plasmas the sheath impendence will be about this value, i.e. a few kilo ohms.

2.2.2 The electrical characteristics of RF plasmas

In RF plasmas (typical excitation frequency of 13.56 MHz), the plasma conductivity σ_p can be introduced by linking the total current density to the electrodes, J_T, to the time-varying electric field, $\hat{E}$, by $J_T = (\sigma_p + i\omega\varepsilon_0)\hat{E}$ with $\sigma_p = (\varepsilon_0\omega_{pe}^2)/(i\omega + \nu_m)$. Here, σ_p is now complex, ε_0 is the permittivity of free space and $\omega_e = (N_{eo}e^2/\varepsilon_0 M_e)^{1/2}$ is the electron plasma frequency. Hence, we can consider the plasma to be either a dielectric or a conductor. For low frequencies ($\omega < \nu_m$, ω_e) we find $\sigma_p \rightarrow \sigma_{dc}$. Here, the DC conductivity is, assuming a cold plasma, given by $\sigma_{dc} = \varepsilon_0\omega_{pe}^2/\nu_m = e^2N_{eo}/M_e\nu_m$. At high frequencies, the situation is complicated and it is often more useful to consider the dielectric constant, ε_p, rather than σ_p (for further details, see Lieberman and Lichtenberg, 1994).

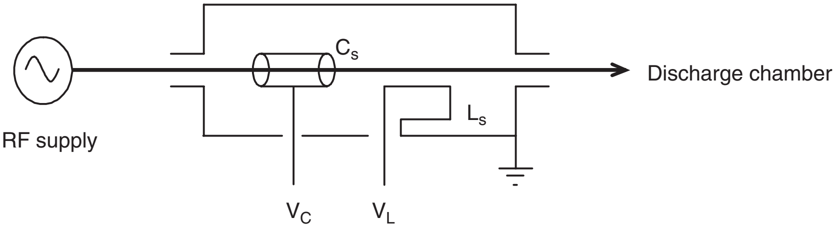
2.2.3 I–V measurements on RF plasmas

Electrical characterisation of a plasma reactor is essential as a starting point for the successful interpretation of discharge processes within the chamber. Since the relationship between the nominal output of the generator and discharge conditions is unknown, a number of methods to infer the electrical characteristics of the plasma have been developed (Sobolewski, 1992; Hargis *et al.*, 1994; Braithwaite, 1997; Bakker *et al.*, 1999; Teuner *et al.*, 1999).

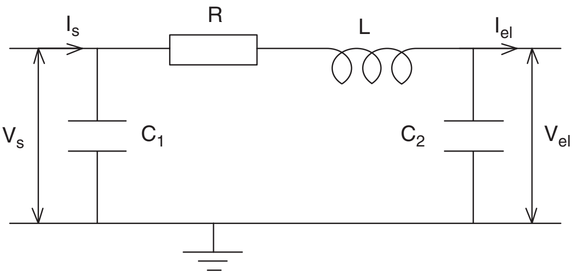
The RF current and voltage probe

Making discharge current and voltage measurements in RF systems is not as straightforward as in d.c. driven plasmas. Nevertheless, the measurements are very important, especially if they can be used to determine a change in the plasma process; for instance, the end point of an etching process, when a change in the chemical nature of a plasma causes a change in the effective impedance of the reactor and therefore a change in the driving electrical characteristics (Dewan *et al.*, 2001; Bose *et al.*, 1994).

Current and voltage sensors have been used on RF discharges in the Gaseous Electronics Conference (GEC) reference cell (Sobolewski, 1992; Hargis *et al.*, 1994) and other vessels (Braithwaite, 1997). They consist of an inductive loop and a cylindrical capacitor housed in a small metal unit inserted in the RF power line and are easily constructed from materials readily available in most laboratories. The probes provide real-time, non-intrusive electrical measurements, but require knowledge of the stray impedance in the power feed-through. An example is shown in Fig. 2.1. The capacitance C_s is that of two coaxial cylinders and the mutual inductance of the loop and power line, L_s, can be calculated from Ampere's law and Faraday's law. The sensor is positioned as close to the driven electrode as possible to minimise the effect of stray impedance. The outputs V_C and V_L are terminated at the 50 Ω input (R_{in}) of a digital oscilloscope, to minimise standing waves in the transmission line. The RF potential of the power line at the sensor, V_s, is calculated from the RC potential divider circuit, $V_s = [1 + (i\omega R_{in}C_s)^{-1}]V_c$. The voltage induced in the loop is related to the current, I_s, in the power line by Faraday's law, $V_L = -L_s(\mathrm{d}I_s/\mathrm{d}t)$, so that $I_s = -(V_L/\omega L_s)$. The current and voltage values at the RF-driven electrode (I_{el} and V_{el}) can be calculated by considering the parasitics in the power line between the I–V sensor and the driving electrode. An equivalent circuit model is shown in Fig. 2.2. The capacitances C_1 and C_2 are determined by the construction of the feed-through and electrode. The length of the current path to the



2.1 Schematic of a current–voltage sensor, consisting of a coaxial capacitor and an inductive loop. V_C and V_L are measured with respect to earth potential.



2.2 An equivalent circuit for the RF power line between the I–V sensor and the powered electrode (Hargis *et al.*, 1994; Braithwaite, 1997).

powered electrode and the return path create the inductance, L. The power line also has a small resistance, R.

The electrical characteristics of the discharge are found by calculating a transfer function for the values measured by the sensor (Hargis *et al.*, 1994). This can be represented by a transmission matrix of complex, frequency-dependent variables, which describe the equivalent LCR network in Fig. 2.2,

$$\begin{bmatrix} V_s \\ I_s \end{bmatrix} = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} V_{el} \\ I_{el} \end{bmatrix} \qquad [2.1]$$

Assuming that the circuit is linear and reciprocal, the determinant of the transmission matrix is unity,

$$ad - bc = 1 \qquad [2.2]$$

Consequently, Equation 2.1 rearranges to form,

$$\begin{bmatrix} V_{el} \\ I_{el} \end{bmatrix} = \begin{bmatrix} d & -b \\ -c & a \end{bmatrix} \begin{bmatrix} V_s \\ I_s \end{bmatrix} \qquad [2.3]$$

The parameters a, b, c, and d can now be obtained from solving Equations 2.1 and 2.2 for open ($I_{el} = 0$) and closed ($V_{el} = 0$) circuit conditions to give,

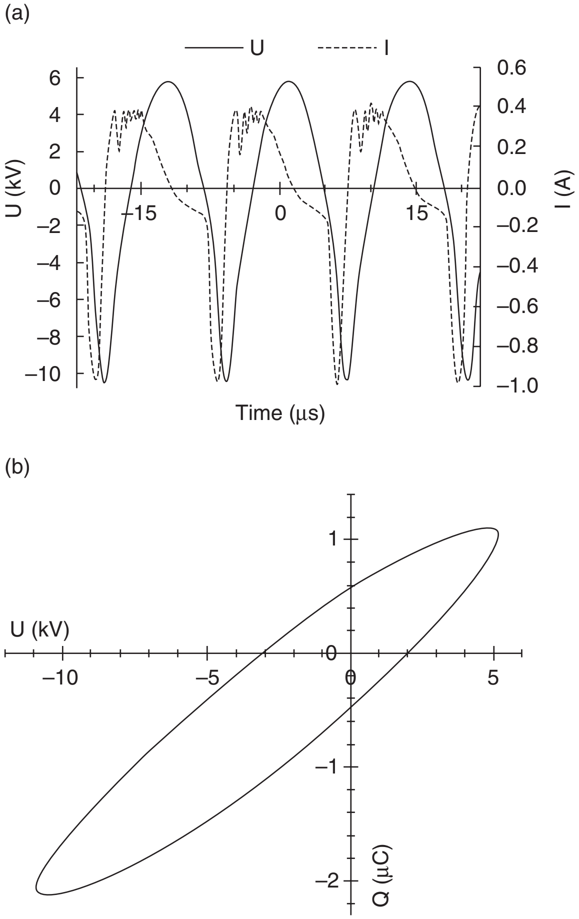
$$a = \left(\frac{V_s}{V_{el}}\right)_{I_{el}=0} \quad c = \left(\frac{I_s}{V_{el}}\right)_{I_{el}=0} \quad \frac{b}{d} = \left(\frac{V_s}{I_{el}}\right)_{V_{el}=0} \qquad [2.4]$$

This is done with the vacuum vessel vented, using a signal generator to provide an input waveform of a few volts amplitude. The powered electrode is securely earthed to create the closed-circuit condition and left electrically floating for open circuit. The voltage and current values at the RF-driven electrode can then be calculated from Equation 2.3. Using the peak values of these parameters, the plasma impedance Z_{el} and rms power dissipated at the electrode P_{el} can be found, since, $Z_{el} = V_{el}/I_{el}$ and $P_{el} = (1/2)V_{el}I_{el}\cos(\phi)$. The angle ϕ is the phase difference between V_{el} and I_{el}. The phase angle between V_s and I_s can be measured directly from the oscilloscope. However, one must remember to compensate for the use of different length probes on the outputs of the sensor, since for RF the phase shift is appreciable, even in short transmission lines.

2.2.4 The current–voltage relationship in high pressure plasmas

In plasmas relevant to the processing of textiles, such as those struck at high pressure, it is important to observe the driving electrical characteristics of the source as an indication of its efficiency and mode of operation. In dielectric barrier discharges (DBD), filamentary and atmospheric-pressure glow discharge (APGD) modes can be distinguished through observation of the characteristic discharge current waveform. For instance, an APGD has only one current peak per half period, whereas a filamentary discharge has many narrow current peaks per half period. Monitoring of the discharge mode has important implications for materials processing. For example, Sira *et al.* (2005) compared the surface properties of polyethylene and polypropylene after surface modification in filamentary and APGD modes. The samples treated in APGD mode were more homogeneous and showed less roughness than those treated in the filamentary mode.

Borcia *et al.* (2005) measured the electrical characteristics of an atmospheric-pressure nitrogen DBD during surface treatment of test polymeric materials (UHMW polyethylene). Figure 2.3(*a*) shows the waveforms of the high voltage used to drive the discharge, and of the discharge current, with the polyethylene film placed on the aluminium cylinder. The power supply was found to generate mixed signals comprising high voltage pulses of variable width and repetition rate superimposed on a continuous sinusoidal waveform. The resulting high-voltage waveform ensured an optimum power level for driving the discharge, with peak-to-peak values in the 10–20 kV range, at a frequency of 80 kHz. Figure 2.3(*b*) shows an example of the Lissajous figures (charge-versus-voltage plot) obtained in the same experiment. These plots can be used to good effect when comparing the discharge process in air and nitrogen environments in terms of the discharge energy and the effect on the discharge parameters (polymer films or woven fabrics placed on the grounded electrode). For instance, the measurements of the electrical parameters in the case of nitrogen flowing through the discharge show values for the energy of the same order of magnitude as in air, that is in the 1–10 mJ range.



2.3 (a) High voltage and current waveforms of the DBD (1.8 mm gap, 80 litres min^{-1} N_2 flow rate). (b) Measured Lissajous figure (Q versus U plot) of the DBD (1.8 mm gap, 80 litres min^{-1} N_2 flow rate) (taken from Borcia *et al.*, 2005).

Lissajous figures have also been used by the same authors for DBD surface treatment of selected polymer films and fibres (Borcia *et al.*, 2003). From these, the energy surface density of the DBD (in mJ cm^{-2}*)* as a function of inter-electrode gap, and the nature of the sample placed on the grounded electrode was determined. Lissajous figures have also been used by Falkenstein and Coogan (1997) to determine the total transferred charge per cycle in a double-barrier discharge. Measurements of the behaviour of single micro-discharges between the metal and glass electrodes for both negative and positive polarities of the metal were made and a theoretical Lissajous figure was constructed, which included stray capacitances, to compare against the experimental figures.

2.3 Electrical plasma diagnostics

Diagnostics based on the electrical properties of plasmas are perhaps the most frequently used methods of determining the local plasma parameters such as electron density, N_{eo}, temperature, T_e, and plasma potential, V_p. Of these, the Langmuir probe is probably the most important but its use is hampered by the complexity of probe theories. This is because there is no general theory that covers all the different types of plasmas. In this section, the theory of Langmuir probes and retarding field analysers is briefly given. For a more comprehensive treatment, the reader is referred to reviews by Demidov *et al.* (2002), Hershkowitz (1989), Chung *et al.* (1975), Swift and Schwar (1970), Schott (1968) and Chen (1965a).

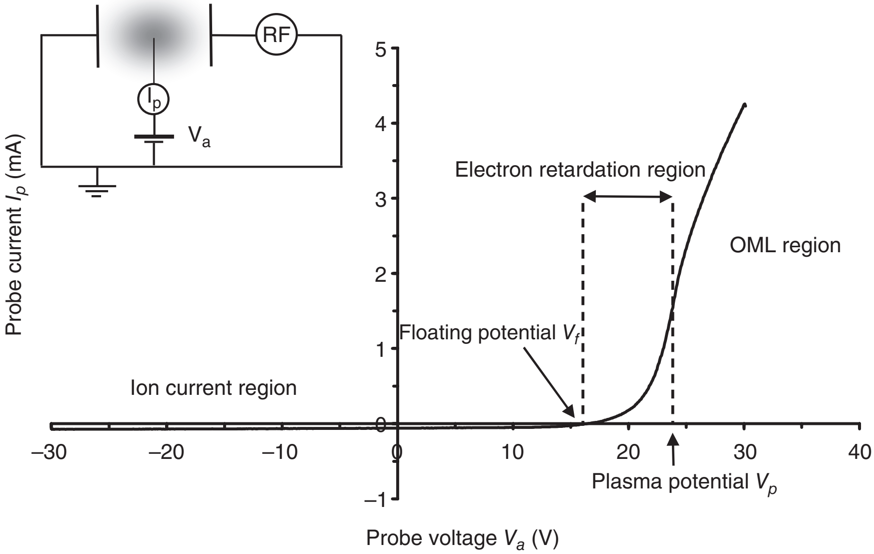
2.3.1 Langmuir probes

Langmuir probes are cylindrical, spherical or planar conductors that disturb the local plasma by the formation of electrostatic sheaths. For large probes (probe radius $r_p >> \lambda_{De}$), these form when the (normalised) potential difference between the plasma and probe, $\eta_a = e(V_a - V_p)/k_BT_e$ with V_a the applied probe voltage, exceeds the Bohm potential, η_B (Riemann, 1991). For $\eta_a < \eta_B \approx -1/2$ (the exact value depends on the ion velocity distribution temperature, T_i) collisionless positive ions are accelerated from the surrounding plasma through a quasi-neutral presheath (roughly equal ion and electron densities) before reaching the Bohm speed where the sheath potential η (= $e(V - V_p)/k_BT_e$) = η_B. Here, the plasma quasi-neutrality breaks down and the rapidly increasing electric field reduces the electron density leaving a net positive space charge region called the sheath. For smaller probes, the position and potential of the boundary between sheath and presheath is not always clearly defined. The sheath thickness, which is a complicated function of η_a, probe geometry and plasma parameters, is usually expressed in units of Debye distance, $\lambda_{De} = (\varepsilon_o k_B T_e/N_{eo}e^2)^{1/2}$. By varying V_a and measuring the probe current, I_p, the probe I–V characteristic is obtained from which the local plasma parameters can be derived.

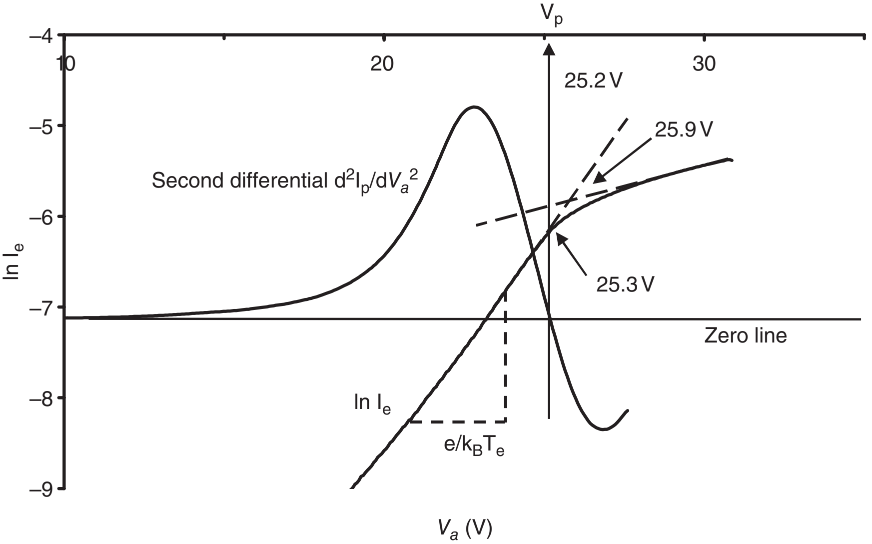
Since probes are necessarily small, to minimise current drain and plasma disturbance, planar probe sheaths can be hemispherical due to edge effects (Ingram *et al.*, 1990). This causes the ion current to continually increase with η_a (<0) due to the expanding non-planar sheath. Guard rings placed around the planar probe can significantly reduce the sheath curvature (Booth *et al.*, 2000), resulting in ion current saturation (i.e. ion current independent of η_a), allowing the simpler planar probe theory to be used. Only spherical and cylindrical probes, which are considerably more complicated, will be considered here.

Elementary Langmuir probe theory

In Fig 2.4 a probe I–V characteristic is shown divided into three regions referred to as the orbital motion limited (OML, $\eta_a > 0$), electron retardation ($\eta_f < \eta_a < 0$) and ion current regions ($\eta_a < \eta_f$). The point of zero current is the probe's floating potential, η_f, which is the potential acquired by an electrically isolated object placed in the plasma. At plasma potential ($\eta_a = 0$), a probe of area A_p collects the random thermal electron current given by $I_{eo} = (1/4)eA_pN_{eo}(8k_BT_e/\pi M_e)^{1/2}$. Since in low-temperature plasmas T_e ($\approx$ 3 eV) >> T_i ($\approx$ 0.03 eV) and $M_i >> M_e$ the ion current is negligible and this equation can be used to obtain the electron density, provided T_e and V_p are known. The plasma potential is usually indicated by the presence of a kink or knee but often this can be difficult to identify and the more accurate derivative method can be used. Here, a maximum in dI_p/dV_a or a zero crossing in d^2I_p/dV_a^2 indicates V_p. Other methods define V_p to be the intersection of extrapolations from the electron retardation and OML regions or the point of deviation from linearity. The latter method is strictly applicable only for Maxwellian electrons. These methods are compared in Fig. 2.5 where it is seen that the inferior extrapolation method overestimates V_p (= 25.2 V) by 0.7 V. The derivatives can be obtained electronically by differentiator circuits (Godyak *et al.*, 1992) or by using the beat method (Amemiya,



2.4 Typical actively compensated Langmuir probe I–V characteristic taken from an argon capacitively coupled RF plasma at low pressure. Analysis of the characteristic is divided into the OML, electron retardation and ion current regions. Insert: Schematic of the discharge circuit including the Langmuir probe.



2.5 Second derivative d^2I_p/dV_a^2 of Fig 2.4 superimposed on a $\ln I_e$–V_a plot. Plasma potential is indicated by the zero-crossing of d^2I_p/dV_a^2 and the deviation from linearity in a $\ln I_e$–V_a plot. In this plot T_e can be also be obtained from the gradient.

1986). They can also be obtained numerically using, for example, Savitzky–Golay filters (Fujita and Yamazaki 1990), finite impulse response filters (Kimura *et al.*, 1991), or Hayden filters (Palop *et al.*, 1995).

In the OML region ($\eta_a > 0$), the ions are rapidly repelled and the electrons are accelerated and collected by the probe. Due to their temperature, the electrons acquire angular momentum in the probe's radial electric field and their trajectories become curved. Some trajectories intersect the probe's surface while others curve around and miss the probe. For electrons that have a Maxwellian velocity distribution far from the probe and for which $\lambda_{en} >> \lambda_{De} >> r_p$ (with the electron-neutral mean free path and r_p the probe radius) this situation is well approximated by the orbital motion limited theory (OML). The electron current is then given by

$$I_e = A_p e N_{eo}\left(\frac{k_B T_e}{2\pi M_e}\right)^{1/2}\left(\frac{2}{\sqrt{\pi}}\right)^{2-s} \qquad [2.5]$$

where $s = 1$ for cylinders and $s = 2$ for spheres. Due to simplifying approximations, this expression is only valid in the cylindrical case, for $|\eta_a| > 2$. A review of OML theory, which is a special case of the more general orbital motion theory (OM) of Laframboise (see Kennedy and Allen, 2003), can be found in Allen (1992a). From this equation, a plot of I_e against $V_a^{s/2}$ gives a straight line from which N_{eo} can be obtained from the gradient. Typically, the electron density obtained by this method is within 10% of the density obtained at V_p (Hopkins and Graham, 1986).

For $\eta_f < \eta_a < 0$, the electrons are gradually repelled and for Maxwellian electrons the current may be written as $I_e = I_{eo}\exp(\eta)$. By subtracting the ion current from the I–V curve and plotting ln I_e against V_a, a straight line of gradient $e/k_B T_e$ is obtained (see Fig 2.5). The temperature is most accurate near to the plasma potential but deviations from linearity caused by, for example, a non-Maxwellian electron distribution, incomplete RF compensation (see section Radio frequency (RF) plasmas) or probe contamination, can result in appreciable errors. Alternatively, T_e can be obtained from the relation $I_e/(dI_e/dV_a) = k_B T_e/e$ (Chen, 2001). Since in most plasmas the electrons are non-Maxwellian (e.g. Godyak *et al.*, 1992), use of these (or other) methods yields the effective or characteristic temperature, T_e. The remarkably linear line, indicating 'Maxwellian' electrons, in the ln I_e–V_a plot (Fig 2.5) is known as Langmuir's paradox. A common method of ion current subtraction is by linear extrapolation from the ion current region ($\eta_a < \eta_f$). However, a better method is to subtract a theoretical fit to the experimental ion current using the appropriate theory of ion collection (see later).

The second derivative of the probe's I_e–V_a characteristic can be used to obtain the electron energy distribution function (EEDF) (Godyak *et al.*, 1992). This is known as the Druyvesteyn method and is applicable to any non-concave probe in an isotropic plasma with collisionless electrons. The EEDF, f(E), can be obtained from:

$$f(E)\big|_{E=e(V_p-V_a)} = -\frac{4}{A_p e^2}\left(\frac{M_e(V_p-V_a)}{2e}\right)^{1/2}\frac{d^2 I_e}{dV_a^2} \qquad [2.6]$$

Numerical integration of this function yields the electron density and the effective temperature can be obtained from $<E> = 3eT_e/2$ where $<E> = M_e <v^2>/2$ is the average electron energy. Note that this method is insensitive for electron energies greater than $e(V_p - V_f)$.

In the ion current region ($\eta_a < \eta_f$), the probe current is dominated by the accelerated positive ions. For collisionless conditions, in which the ion-neutral mean free path $\lambda_{in} >> \lambda_{De}$, the ion current can be approximated by the OML theory (Equation 2.5 with subscript *e* substituted for *i*). This theory is only applicable to small cylindrical ($r_p/\lambda_{De} \leq 3$ for $\eta_a \leq -10$) or spherical probes ($r_p << \lambda_{De}$). For larger probes parametric expressions approximating the numerical results of Laframboise (Chen, 2001) can be used. In another approach, Allen *et al.* (1957, ABR) (for spheres) and later Chen (1965b) (for cylinders) developed a collisionless theory in which cold ions ($T_i = 0$) are accelerated radially along the electric field lines. By fitting the theoretical ion current to the measured one, the electron density, as fitting parameter, can be obtained. Many studies have shown disagreement between the OM and ABR theories (Hopkins and Graham, 1986; Sudit and Woods, 1994; Chen, 2001) with the ABR theory giving better agreement with the knee density usually to within a factor of 2 (Passoth *et al.*, 1997; Bryant *et al.*, 2001a). This has been attributed to ion-neutral collisions destroying orbital motion and promoting radial motion, increasing the ion current to the probe (Stangeby and Allen, 1971). A criterion for the applicability of orbital motion theories with finite λ_{in} has been suggested by Chen (1965b), Shih and Levi (1971) and Annaratone *et al.* (1992). For weakly to moderately collisional sheaths ($\lambda_{in} \sim \lambda_{De}$) other theories have been developed in which collisions have been incorporated into spherical ABR theory (Self and Shih, 1968), modeled as a perturbation (Shih and Levi, 1971) resulting in a correction factor, or considered at a kinetic level (Chou *et al.*, 1966; Tichý *et al.*, 1994). At higher pressures, the sheath is fully collisional ($\lambda_{in} << \lambda_{De}$) and ion motion is governed by diffusion and mobility (Su and Lam, 1963; Cohen, 1963 for spheres; Kamitsuma and Teii, 1982 for cylinders).

Radio frequency (RF) plasmas

In RF plasmas, the plasma potential oscillates, resulting in a time-dependent voltage drop across the sheath. This distorts the I–V characteristic, increasing the time-averaged electron current in the retardation region and shifting the characteristic towards the negative voltages, so that conventional probe theory cannot be used (Boschi and Magistrelli, 1963). In general, there are two methods for removing the RF voltage and associated harmonics across the probe sheath: (i) use of a passive probe in which a series of LC resonant filters (Chatterton *et al.*, 1991) or low-pass filters (Annaratone and Braithwaite, 1991) are placed in the probe circuit to force the probe to follow the instantaneous plasma fluctuations; or (ii) use of an active probe in which phase and amplitude matched RF voltage waveforms are applied to the probe tip (Dyson *et al.*, 2000). This technique has the advantage of providing local information of the phase and magnitude of the plasma harmonics. Once the probe is compensated, conventional Langmuir probe theory can then be used to extract the plasma parameters.

Electronegative plasmas

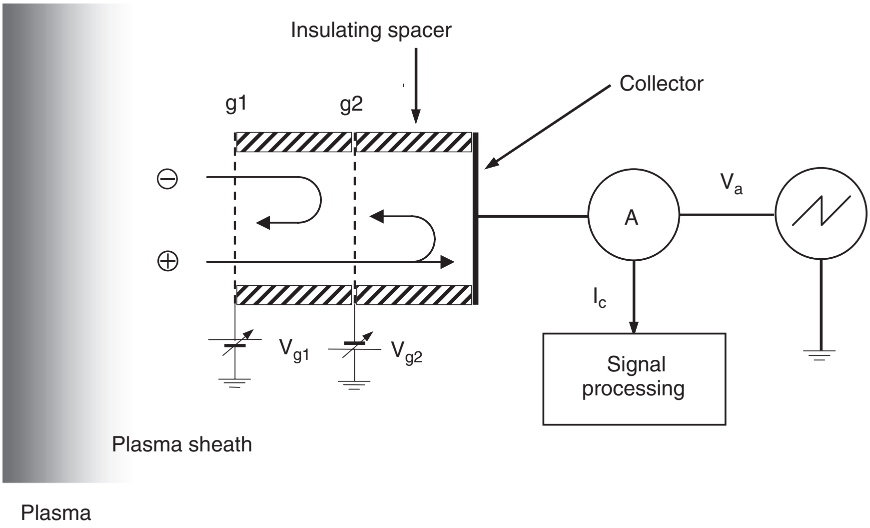
Obtaining the negative ion density, N_{no}, and temperature, T_n, directly from the measured I–V curve is made difficult because $T_e >> T_n \sim 0.1$ eV so that the negative ion current is negligible in both the retardation and OML regions. For collisionless sheaths and critical ratios $\alpha_c = N_{no}/N_{eo} \approx 2$ or less, the presheath is dominated by electrons and positive ions (electropositive) and the presence of negative ions cannot be detected by the probe. For ratios greater than $\alpha_c \approx 2$ and $\gamma_c = T_e/T_n \approx 10$ (Braithwaite and Allen, 1988), the Bohm potential is reduced to approximately $\eta_B \approx -1/2\gamma$ and the presheath is populated by electrons, positive and negative ions (electronegative). In the presence of ion-neutral collisions, α_c increases with pressure but γ_c remains constant (Bryant, 2003). For $\alpha_c < \alpha < \alpha_M$, sheath instabilities can form (Kono, 2003), which invalidates the use of the probe. The instabilities are not present for $\alpha > \alpha_M$ and the positive ion current, which is proportional to $\alpha\gamma^{-1/2}$ (Bryant *et al.*, 2001b), can then be used for diagnostics. For an ideal planar probe (no edge effects), the ratio of electron to ion saturation currents (current ratio method) can then be used to give α provided γ is known (Amemiya, 1990). Chabert *et al.* (1999) used a combination of planar and cylindrical Langmuir probes to determine the negative ion density by this method in an SF_6 helicon reactor. By extending the ABR theory to include negative ions, Amemiya *et al.* (1999) suggested fitting the theoretical ion current characteristic to an experimental curve to determine α (if γ and N_{eo} are known). The method was applied experimentally, after correcting for ion-neutral collisions, by Bryant *et al.* (2001b) in a pure RF oxygen plasma. Negative ions, when present in sufficient quantities, can cause T_e to increase due to electron losses by attachment and depress the low-energy part of the EEDF, revealing the negative ion EDF. Under these conditions, a modified Druyvesteyn method can be used to measure both α and γ simultaneously (Amemiya and Yasuda, 1997).

Magnetised plasmas

In magnetic fields, charged particles gyrate around magnetic field lines at the Larmor radius $r_{Li,e} = M_{i,e}\, v_\perp/qB$, where $v_\perp$ is the angular velocity and B the magnetic field. Motion parallel to field lines is unaffected but motion across field lines is impeded due to gyration. This causes anisotropy in the particle's velocity distribution (Aikawa, 1976), introducing additional complexity into probe theory and analysis. In weakly collisional conditions, the effective mean free path $\lambda_{in,en}$ across the magnetic field is of the order of the Larmor radius, making the problem collisional even when $r_{Li,e} < r_p$ and $\lambda_{in,en} >> r_p$. Generally, probe operation can be characterised by the parameters $\max(\lambda_{De}, r_p)/r_{Li,e}$ and B/pressure (Chung *et al.*, 1975). At high pressures, $\lambda_{in,en} < r_{Li,e}$ and the action of the B-field is reduced by collisions (Niyogi and Cohen, 1973). For weak B-fields, $\max(\lambda_{De}, r_p)/r_{Li,e} << 1$ and particle motion are unaffected by the B-field and zero-magnetic field probe theory can be used. For moderate B-fields, $\max(\lambda_{De}, r_p)/r_{Le} \sim 1$ (with $\max(\lambda_{De}, r_p)/r_{Li} << 1$) and electron gyration can no longer be neglected. The preferential motion of electrons along the field lines causes the electron current at plasma potential and in the retardation region to be reduced, resulting in rounding of the knee. As η_a (<0) is increased, the probe characteristic becomes less distorted as the higher energy electrons have larger Larmor radii (Sanmartin, 1970; Sonmor and Laframboise, 1991). Use of standard probe analysis in this region causes T_e to be overestimated and V_p underestimated. For cylindrical and planar probes, the reduction is minimal when the probe's axis is perpendicular to the field lines (Rubinstein and Laframboise, 1983; Thompson and Bradley, 2001). The EEDF can be inferred, for cylindrical symmetry about the B-field vector, by employing a rotational planar probe (Klagge and Lunk, 1991; Mezentsev *et al.*, 1988). In the ion current region the motion of unmagnetised ions can be described as for the zero-magnetic field case (Passoth *et al.*, 1997).

2.3.2 The retarding field analyser (RFA)

The RFA can be immersed in the plasma bulk as a gridded probe or mounted on one of the electrodes (or substrate) and consists of a series of grids and a collector plate (see Fig 2.6). Gridded probes can be used to measure the anisotropy of T_e and the EEDF. To avoid drawing excessive electron currents and perturbing the plasma, the first grid, g1, is usually biased at a potential $V_{g1} < V_p$ (Ingram *et al.*, 1990). Mounted RFAs, which are usually used to measure the ion energy distribution function (IEDF) at electrodes, have g1 biased at the electrode potential to avoid perturbing the adjacent sheath. Generally, two modes of operation, filter and normal mode,



2.6 Schematic of a RFA and external circuit. The first grid, g1, is biased at the electrode potential (mounted RFA) or biased slightly below plasma potential (gridded probe). In normal mode, plasma electrons are repelled by g2 while the positive ions are accelerated through g2 and are then selectively repelled, according to their energy, by a ramping retardation potential applied to the collector.

are possible with the remaining grids and collector. Ingram *et al.* (1990) concluded that filter mode exhibited more disadvantages than normal mode. In this mode, the second grid, g2, is used to repel the unwanted plasma species and a linear voltage ramp, V_a, is applied to the collector to filter the remaining species. In gridded probes $V_{g2} > V_p$ (by several volts) to repel the positive ions whereas in mounted RFAs V_{g2} can be negative ($<-10T_e$) to reject the electrons or positive (> maximum ion energy) to sample the high energy part of the EEDF (Ingram and Braithwaite, 1988). For RFAs with g1 grounded, the maximum ion energy can be used to measure V_p (Ingram and Braithwaite, 1988) and T_e (Sowa *et al.*, 2002) if the plasma sheath is suffiently collisionless.

In general, for an ideal planar RFA of area A, the particle velocity distribution function (VDF) as sampled at g1, $f_1(v_1)$, can be obtained from the first derivative of the I–V characteristic (see Ingram and Braithwaite, 1988) by

$$\frac{\mathrm{d}I_c}{\mathrm{d}V_c} = -T_t A \sum_{i=1}^{N} \frac{q_i^2 f_1^i(v_1)}{M_i} \qquad [2.7]$$

with $V_c = V_a - V_{g1}$; q_i the charge for the ith species; and $T_t = T_1 T_2$, the total grid transmission. Note that, for mounted RFAs, the observed VDF, $f_1^o(v_1)$, is a weighted sum over N ionic species. Since a plot of $\mathrm{d}I_c/\mathrm{d}V_c$ against V_c is a plot of $(-T_t A q^2/M) f_1^o(v_1)$ against $(M/2e)v_1^2$, the EDF can be obtained by plotting $(\mathrm{d}I/\mathrm{d}V_c)/V_c^{1/2}$ against V_c (Allen, 1992b). Alternatively, the velocity distribution may be obtained by plotting $\mathrm{d}I/\mathrm{d}V_c$ against $V_c^{1/2}$, thereby avoiding the singularity at $V_c = 0$. For gridded probes, the EDF must be shifted by an amount $V_p - V_{g1}$ to obtain the EEDF.

In designing an RFA, the grid apertures of g1 should be of the order of, or less than, λ_{De} to prevent plasma penetrating through the grid and to minimise distortion of the sheath's electric field (Edelberg *et al.*, 1999a). To prevent ion–neutral collisions in the RFA from causing spurious signals, the overall thickness should be less than λ_{in}. This can be accomplished by differential pumping (Flender and Wiesemann, 1994) or by design (Ingram and Braithwaite, 1988, Sowa *et al.*, 2002). The collector is usually tantalum or tungsten to reduce secondary electron emission (by ion bombardment), which can be reduced further by inserting additional grids (Böhm and Perrin, 1993; Kortshagen and Zethoff, 1995). The energy resolution of the RFA is limited by defocusing of ions or electrons in the vicinity of the grid apertures (Simpson, 1961) and by space charge effects (Donoso and Martin, 1990; Honzawa *et al.*, 1993). In particular, defocusing is caused by distortion of the field lines leading to a reduction in the translational velocity component and distorting the EDF (Edelberg *et al.*, 1999a). A number of studies have shown the resolution to be a complicated function of grid separation, wire diameter and aperture radius (Sakai and Katsumata, 1985; Donoso and Martin, 1986) and that it can be improved by using additional grids (Enloe and Shell, 1992). Other possible sources of error that may distort the EDF are due to the particle collection by grid apertures (Moskalev, 1970) and the finite size of the analyser (DeNeef and Theiss, 1979).

Other RFA designs can measure the ion angle distribution at grounded (Liu *et al.*, 1990) or driven (Woodworth *et al.*, 2002) electrodes: IEDFs at driven electrodes (Edelberg *et al.*, 1999b), and three-dimensional EDFs in the bulk plasma by rotating a conventional gridded probe (Iwama *et al.*, 1988) or by using a directional analyser (Stenzel *et al.*, 1983). Finally, the RFA can be combined with a quadrupole mass spectrometer to obtain mass and energy resolved IEDFs (Thompson *et al.*, 1986).

2.3.3 Other probe techniques

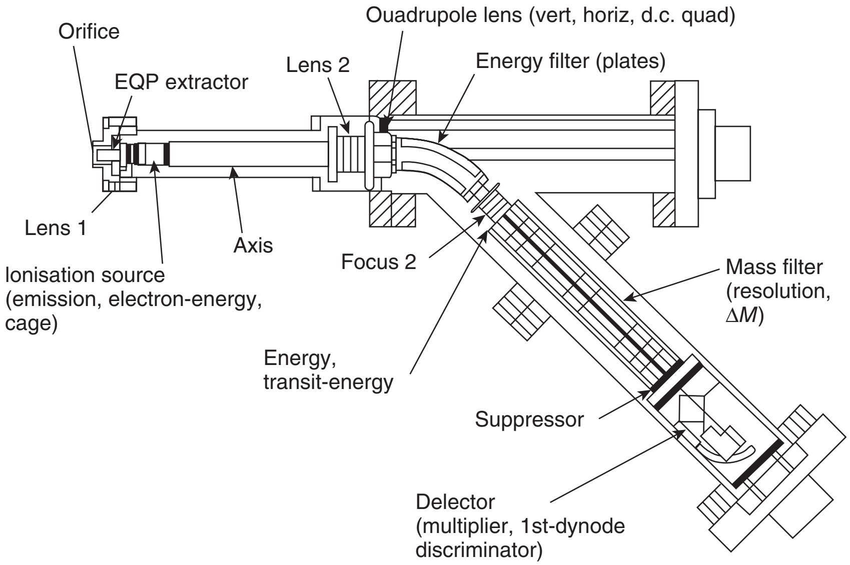
With reference to Fig. 2.4 (insert), the Langmuir probe forms part of the external discharge circuit with the restriction that $A_p/A_{gnd} << (2\pi M_e/M_i)^{1/2}$ (Ingram *et al.*, 1990), with A_{gnd} being the total grounded area, to minimise perturbation of the plasma. In electrodeless discharges, such as inductively coupled plasmas, there is insufficient grounded surface area so that the Langmuir probe invariably perturbs the plasma. By using floating probe techniques such as double (Welzel *et al.*, 2004), direct-display triple (Alami *et al.*, 2005, Kamitsuma *et al.,* 1977), emissive (Bradley *et al.*, 2004) or, more recently, hairpin resonator probes (Piejak *et al.*, 2005) this can be avoided. These probes have the additional advantage of following the instantaneous plasma fluctuations and are ideal for time-resolved plasma diagnostics.

2.4 Plasma mass spectrometry

Plasma mass spectrometry is a well-developed technique that provides information on the identity of the neutral and charged species present in a discharge, and their relative fluxes to a material surface or substrate. The technique is also an ideal tool for understanding the behaviour of plasmas with complicated mixtures of chemical precursors. There are many excellent and detailed reviews of this technique as applied to plasma discharges; for instance, Zeuner (2004) and Jarvis *et al.* (1990). We only discuss the fundamentals here, highlighting how mass spectrometry is used in the areas of residual gas, neutral and ion plasma analysis.

2.4.1 Commercial mass–energy spectrometers

A typical mass–energy spectrometer is shown in Fig. 2.7. This example is the Hiden electrostatic quadrupole plasma (EQP) 300 mass spectrometer



2.7 Schematic of the Hiden Analytical EQP300 mass spectrometer apparatus (Hiden).

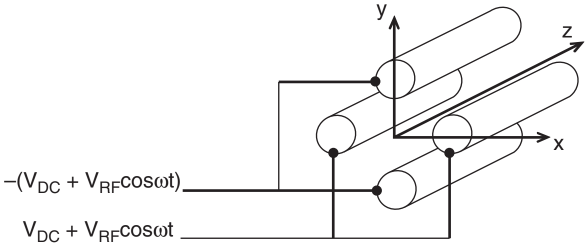
(Hiden Analytical Ltd). Other examples include the Balzers PPM421 plasma monitor as used by Kusano *et al.* The EQP is capable of resolving particles of mass up to 300 AMU and can measure the energies of positive and negative ions over a range of ±1000 eV with respect to ground. Sampling is done through an orifice, typically 10 to 500 microns in diameter, which is in contact with the plasma via the plasma sheath. This is a region of space-charge that exists between the bulk plasma and a surface, which is at a different potential to the plasma (Lieberman and Lichtenberg, 1994). To minimise distortion of the sheath electric field, the orifice diameter must be less than the Debye length. However, in the absence of an electric field downstream from the plasma the sheath electric field can penetrate through the orifice (Liu *et al.*, 1990). This causes low energy ions to be defocused into the orifice walls or lost in the field-free region. In the Hiden system the first lens, the extractor, is typically biased (negatively) up to several tens of volts relative to the orifice potential. The electric field then reduces field penetration and focuses the ions into the remaining lenses. Computer control is used to set voltages on the lenses and electrodes inside the instrument, which number around twenty. Groups of these lenses focus the ion beam at each of the mass and energy analysis stages. The latter is achieved with a 45° electrostatic cylinder sector arrangement (Hiden). Other energy selection methods, including cylindrical mirror analysers, are discussed in more detail by Zeuner (2004). Once past the analysis stages, the ion beam is converted into an electrical signal by either a Faraday cup or a high gain channeltron (continuous dynode) multiplier.

Neutral species entering the spectrometer are ionised, before the analysis stages, by an electron impact ion source (e.g. see Brink, 1966), situated close to sampling orifice. The ionised particles are extracted from the source by a system of electrically biased lenses. Typical electron energies of 70 eV in the source can cause molecules, particularly large organic molecules, to split into smaller ionised fragments. The additional peaks appear in the mass spectra as fragmentation patterns whose parent molecules can be identified by comparison to a database. When no fill gas is present in the plasma chamber, the ion source can be used for troubleshooting and calibration of the mass and energy analysis stages. To analyse only plasmaion species, the ion source is switched off.

The mass spectrometer housing is pumped to pressures below 10^{-4} Pa to avoid damage to the channeltron detector and ion source filaments. The low-pressure environment also ensures that there are insignificant collisions of ionised species (e.g. scattering, molecular dissociation, reactions involving radicals, etc.) en route to the detector. Additionally, the small orifice allows plasmas of pressures up to about 200 Pa to be sampled. At higher pressures, a two- or three-stage pressure reduction system is necessary (e.g. Singh *et al.*, 1999).

2.4.2 The quadrupole mass filter

The mass filter commonly used in many plasma research laboratories is the quadrupole (Dawson, 1976). As the name suggests, four parallel rods form the active part of the mass filter (see Fig. 2.8). Ideally, the rod's cross-section should be hyperbolic but, in practice, cylindrical geometry is used, since this is easier to manufacture and the loss in resolution is acceptable. By applying d.c. and RF voltages (V_{DC} and V_{RF}) to the rods, the time-varying electric fields will cause the ions to oscillate as they traverse the filter, resulting in a mass filtering action. Ions with the critical mass to charge (M/q) ratio will



2.8 Schematic of a quadrupole mass filter. Ions pass through in the z-direction.

have stable trajectories and pass through the filter. For others, the oscillation amplitude increases until they are absorbed by the walls or rods (McDowell, 1963; White and Wood, 1986). The critical M/q ratio depends only on the ratio $k = V_{DC}/V_{RF}$, so that a mass spectrum is obtained by scanning through the M/q values on a scan line (with $V_{DC} = kV_{RF}$) for each value of k. The mass resolution is given by $\Delta M = k_1E/f^2L^2$ with k_1 a constant, f the RF frequency, L the quadrupole length and E the ion entrance energy. Higher resolution can be achieved by using longer electrodes but their uniformity and positioning are critical to the accuracy of the instrument. Also, the transmission decreases with increasing resolution. In practice, the position of entry, the ion's radial velocity component and the presence of fringing electric fields also affect the filtering action. The incident ion beam is then restricted at the analyser's entrance by a circular aperture. Fringing fields are minimised by use of additional filters positioned in-front or behind the quadrupole.

2.4.3 Residual gas analysis (RGA)

In RGA analysis, the spectrometer is used to sample the neutral species from an evacuated plasma chamber. The mass spectrum represents the residual gas (i.e. impurities) that originates from vacuum seal leaks and out-gassing from the chamber walls and spectrometer housing. For some plasma processes the presence of these impurities is detrimental, so this information can be invaluable. RGA analysis can also be used to trace sources of leaks. This is usually done by squirting, for instance, helium around vacuum seals outside the chamber with leaks detected by the spectrometer as sudden increases in the helium counts. The partial pressure of gas, effusing through the orifice, at the ion source is given by $P_L = P_{ch}\,[R^2/(R^2 + L)]$ with R the orifice radius, L the distance from the orifice and P_{ch} the plasma chamber pressure (Coburn and Kay, 1971). To ensure that the partial pressure of residual gas from the spectrometer housing, P_{sh}, is negligible during RGA analysis, we require $P_L >> P_{sh}$.

2.4.4 Neutral plasma analysis

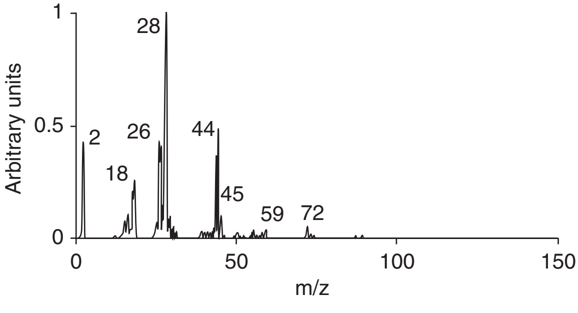
By applying a large positive potential (> the plasma potential V_p) to the extractor (Hiden), the positive plasma ions are repelled, allowing the neutral plasma species to be analysed. This technique is used, for example, to monitor changes in gas composition, identify plasma fragmentation products and differentiate between neutrals that have originated from the walls and from the processed work piece, and those formed in the plasma itself. In some environments, the neutral plasma spectrum plasma can be complex in nature, consisting of many tens if not hundreds of different masses, with the equilibrium concentrations a sensitive function of the discharge parameters (e.g. see Haddow *et al.*, 2000). As an example, Fig. 2.9 shows the neutral mass spectra taken in a continuous wave 13.56 MHz plasma polymerising discharge run in acrylic acid (Barton *et al.*, 2003).

Threshold ionisation mass spectrometry

Through variation of the electron energy in the ion source, near the ionisation potential of the species under study, it is possible to identify radical species in the plasma. This technique has been used to good effect in the identification of radicals such a CF_3 and CF_2 in CF_4 RF plasmas (Schwarzenbach *et al.*, 1997). Any detected ionised species could have come from dissociative ionisation of a molecule when the electron impact energy exceeds its ionisation potential. Since dissociative ionisation requires more energy to be transferred by the electron, the energy for this is higher than the ionisation of the radical by approximately the binding energy. With a good electron energy resolution in the ion source, it is possible to differentiate between ions produced from radicals and from dissociation. This technique is best used by comparing signals generated when the plasma is off (only process gas) and when it is on (gas plus ionisation of radicals). As identified in Biederman (2004), this technique has been used to detect SiH_x radicals (Kae-Nune *et al.*, 1995; Robertson and Gallagher, 1986), CF_x radicals (Pecher and Jacob, 1998) and CH_x radicals (Singh *et al.*, 1999).

Electron attachment mass spectrometry

In this technique, negative ions are created in the ion source from electron attachment onto electronegative species such as fluorine, oxygen and



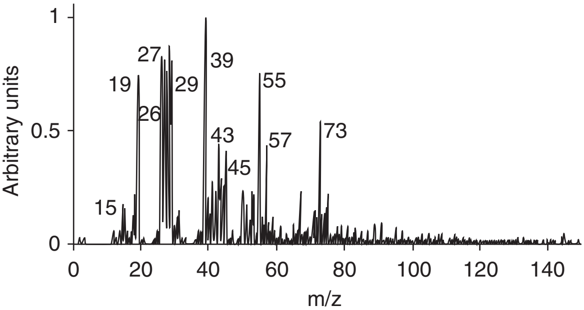
2.9 Electron impact (neutral species) mass spectrum of 5 W plasma, without applied RF substrate bias. m/z: 26 = $C_2H_2^+$; 28 = $C_2H_4^+$, 28 = OC^+, 28 = N_2^+; 44 = $C_2OH_4^+$, 44 = CO_2^+; 72 = $C_3H_4O_2^+$. There is a detectable signal in the neutral monomer at mass 72; however, the largest signals come from fragments of this molecule (taken from Barton *et al.*, 2003).

chlorine containing process gases, through dissociative attachment $AB + e^- \rightarrow A^- + B$ (Stoffels *et al.*, 1998; Rees *et al.*, 1998). The electron energy is set low, between 0 and 10 eV, in order to coincide with the resonance cross-section. Also, very limited fragmentation of the parent negative ion occurs, so a given molecule yields only a few different negative ions. This facilitates identification of components in a gas mixture. It is particularly advantageous for detection of large, fragile molecules, which break up after ionisation, but can be easily transformed into large negative ions.

2.4.5 Positive ion analysis

By turning off the ion source and using the energy filter in combination with the quadrupole, the instrument can sample plasma ions directly. The ions, after traversing the sheath adjacent to the orifice, arrive with a distribution of energies. The detected ion energy represents the potential at which the ions underwent their last collision process. These processes include in-elastic interactions such as ionisation, resonant (i.e. $A^+_{\text{fast}} + A_{\text{slow}} \rightarrow A_{\text{fast}} + A^+_{\text{slow}}$) and non-resonant (i.e. $A^+_{\text{fast}} + B_{\text{slow}} \rightarrow A_{\text{fast}} + B^+_{\text{slow}}$) charge transfer and elastic interactions such as polarisation scattering. Fast neutrals generated by charge transfer collisions have been observed by Janes and Börnig (1993). In low pressure d.c. plasmas, the ion energy distribution function (IEDF) has a single peak near to the plasma potential where most of the ionisation takes place. For collisionless sheaths, the peak width (full width at half maximum) is proportional to the electron temperature and the plasma potential is determined by the maximum ion energy. As the sheath becomes collisional, a tail then extends to the lower energies (Lieberman and Lichtenberg, 1994). However, in RF excited plasmas (e.g. those excited at 13.56 MHz), the sheath potential drop and its width vary approximately sinusoidally (usually higher harmonics are present) at the driving frequency. In some situations this manifests itself in the IEDF being shifted to higher energies (Riemann, 1989), becoming also wider and often accompanied with peak splitting (see review by Kawamura *et al.*, 1999). The modification of the IEDF by RF bias was used by Barton *et al.* (2000) to change the ion flux of argon ions bombarding a polymeric surface.

By selecting ion energies corresponding to the IEDF peak (near to V_p), the bulk plasma positive ion mass spectrum can be measured. Figure 2.10 shows the ion mass spectra in the same polymerising discharge as shown in Fig. 2.9. The spectrum reveals the complex nature of the positive ion species in the discharge. Plasma ion mass spectrometry has also been used in a pulsed glow discharge operated in CH_4–argon mixtures, for the treatment of PVDF in textile modification applications (Vohrer *et al.*, 1998), to observe the long-term time dependence of H_2F^+. As polymerisation takes place when the plasma is turned off, a film covers the substrate and the usually ablated H_2F^+ signal in the mass spectrum is subsequently reduced.



2.10 The positive ion mass scan at 5W without applied RF bias. We assign the masses to the following; 15 = CH_3^+; 19 = OH_3^+; 26 = $C_2H_2^+$; 27 = $C_2H_3^+$; 29 = $C_2H_5^+$, COH^+; 43 = $C_2OH_3^+$; 45 = $C_2OH_5^+$; 59 = $C_3OH_7^+$; 73 = $C_3O_2H_5^+$. (taken from Barton *et al.*, 2000).

2.4.6 Negative ion analysis

Due to their low temperature (≈ 0.1 eV), negative ions created in the plasma bulk are usually confined to the discharge region by the boundary sheaths. However, in sufficient quantities their presence can affect the sheaths, leading to a reduction of the positive ion fluxes to the electrode and spectrometer (Lieberman and Lichtenberg, 1994). There are a number of techniques of extracting the bulk plasma negative ions. One such technique involves modulating the applied power (e.g. RF excitation) in such a way as to depress the local plasma potential below that of the extractor electrode (Howling *et al.*, 1993a). In an RF plasma, a positively biased orifice is used to attract the negative ions (Sasaki *et al.*, 1997). In other methods, the plasma potential is modulated with the electrode kept at a fixed bias, e.g. in pulsed (10 Hz–10 kHz) square wave RF silane discharges (Howling *et al.*, 1993b), and in other similar plasmas, e.g. by Overzet *et al.* (1989). In some plasmas, for example in reactive magnetron sputtering of metals in O_2 atmospheres, the negative ions (O^- and O_2^-) have enough intrinsic energy to overcome the small negative repelling potential of the plasma sheath at the orifice to be detected directly (Mišina *et al.*, 2003; Zeuner *et al.*, 1998). In an asymmetric capacitively coupled RF plasma, Zeuner *et al.* (1996) observed negative ions, at the grounded electrode, of energies comparable to the d.c. bias on the driven electrode. They concluded that the negative ions were formed in the vicinity of the driven electrode and had acquired enough energy in the driven electrode sheath to cross the plasma and reach the grounded electrode.

2.4.7 Time-resolved mass spectrometry

Since many discharges are now operated in the pulse regime, it is becoming increasingly important to understand the time variation of the concentrations and energies of ionic species. This is particularly important for the low-pressure pulsed plasma polymerisation of organic monomers to form thin films (Han *et al.*, 1998) and in the reactive pulsed magnetron sputtering of ceramic films (Vlček *et al.*, 2004).

There are essentially two methods to achieve time-resolution: (i) allow ions to continually enter the instrument and gate the detector signal (Hiden) or (ii) physically or electrically gate the ions entering the instrument and detect the arriving ion packets at the detector. The latter has been achieved on RF plasma reactors in inert gases and also in polymerising gases such as acrylic acid (Voronin *et al.*, 2005), and on magnetrons (Karkari *et al.*, 2002). In the latter, a time resolution of 4 μs was achieved using electronic gating.

2.5 Optical emission spectroscopy

In general, radiation emitted from plasma sources is either continuum or line radiation. Continuum radiation results from free–free (e.g. Bremsstrahlung) and free–bound (e.g. radiative recombination) interactions with the free electrons. In both cases the radiation depends, amongst other factors, on the continuous distribution of electron energies in the plasma. Line radiation results from photons emitted by electron transitions (bound–bound) between the discrete energy levels of the parent atom, molecule or ion. An electron in an upper level of energy, E_p, can spontaneously decay to a lower level, E_q, emitting a photon of energy $h\nu_{p,q} = E_p - E_q$. The spontaneous transition probability per second (one of the Einstein coefficients) is denoted by $A_{p,q}$ and its reciprocal is the mean life-time of the state. The number of electrons in a given level is determined by a balance between 'upward' processes (ionisation, excitation) and 'downward' processes (recombination, de-excitation). Plasmas in which radiative processes dominate (e.g. photo-ionisation, radiative recombination) are called radiative plasmas whereas collisional processes (e.g. impact ionisation and excitation) dominate in collisional plasmas, and this is usually the case in technological plasmas.

Plasmas in which radiation is completely re-absorbed (resonant radiation) are optically thick and have a large optical depth. The observed radiation provides information about the outer plasma regions only. In optically thin plasmas, re-absorption is insignificant so that radiation from the inner regions of the plasma can escape. Radiation from optically thin plasmas offers insight into the dynamic and complicated atomic processes taking place deep within the plasma volume. The observed intensity (defined as the radiant energy dE emanating from an area dA in a time dt into a solid angle dΩ and has units of $\mathrm{J\,s^{-1}\,m^{-2}\,sr^{-1}}$) is then related to the electron density N_{p}^{z} of level p in a radiator of ionisation stage z (where $z = 0$ is neutral, 1 is singly ionised, etc.), the transition probability $A_{\mathrm{p,q}}$ and the thickness (D) of the plasma volume being observed:

$$I_{\mathrm{p,q}}^{z} = \frac{g(\nu_{\mathrm{p,q}})}{4\pi}\int_{0}^{D} N_{\mathrm{p}}^{z} A_{\mathrm{p,q}} h\nu_{\mathrm{p,q}}\,\mathrm{d}x \qquad [2.8]$$

Here, $g(\nu_{\mathrm{p,q}}) = TC_{\mathrm{f}}$ with C_{f} the wavelength dependant spectrometer calibration factor and T the window (or filter) transmission. The calibration factor is usually determined from a known black or grey body radiator such as a tungsten lamp. Usually it is necessary to assume a homogeneous plasma of depth D along the line-of-sight so that Equation 2.8 simplifies to $I_{\mathrm{p,q}}^{z} = [g(\nu_{\mathrm{p,q}})/4\pi]N_{\mathrm{p}}^{z}A_{\mathrm{p,q}}h\nu_{\mathrm{p,q}}D$. By comparison of the measured intensity–wavelength spectrum with a database of known emission lines, radical plasma species can be identified (e.g. Chaivan *et al.*, 2005). Since $I_{\mathrm{p,q}}^{z} \propto N_{\mathrm{p}}^{z}$, a qualitative measure of the radical density over a range of plasma conditions can also be obtained (e.g. Raffaele *et al.*, 2003).

This section attempts to cover some of the important aspects of optical emission spectroscopy (OES) and its use as a diagnostic. More thorough treatments can be found in McWhirter (1965), Cooper (1966), Richter (1968) and Lochte-Holtgreven (1968). For line broadening mechanisms, Wiese (1965) and Traving (1968) provide a comprehensive review. Other topics such as trace rare gases OES (Donnelly, 2004) and atmospheric plasma OES (Laux *et al.*, 2003) are treated elsewhere. Spectroscopic data useful to OES can be obtained from the NIST database (http://www.nist.gov).

2.5.1 Plasma models

To extract meaningful information from intensity measurements, spectroscopic models, which attempt to describe the main atomic processes in a plasma volume, are used. From these models, relationships between measured spectroscopic quantities such as line ratios or absolute intensities of selected emission lines enable the plasma parameters to be determined. In the following models, it is convenient to assume that the electrons have a Maxwellian energy distribution. Since many plasmas are non-Maxwellian, the electron temperature, T_{e}, is a characteristic temperature. Finally, it is assumed that the plasma being modelled is optically thin.

Steady-state corona model

At low pressures and electron plasma densities, N_{eo}, three-body recombination ($\propto N_{\mathrm{eo}}^2$) and collisional de-excitation rates can become less than radiative recombination ($\propto N_{\mathrm{eo}}$) and spontaneous emission. Also, collisional ionisation and excitation rates can dominate over radiative excitation and photo-ionisation. Under these conditions, collisional excitation (and ionisation) is balanced by spontaneous emission (and radiative recombination) to any lower level. Further simplification is achieved by considering only the dominant excitations from ground states and transitions between ground state ionisation stages. Finally, steady state is ensured by the population densities being in equilibrium with the slowly varying plasma parameters. Corona equilibrium is then defined by:

$$N_{\mathrm{eo}} N_{\mathrm{g}}^{\mathrm{z}} X(T_{\mathrm{e}}, g, p) = N_{\mathrm{p}}^{\mathrm{z}} \sum_{\mathrm{q<p}} A(p, q) \qquad [2.9]$$

$$N_{\mathrm{eo}} N_{\mathrm{g}}^{\mathrm{z}} S(T_{\mathrm{e}}, z, g) = N_{\mathrm{eo}} N_{\mathrm{g}}^{\mathrm{z+1}} \alpha(T_{\mathrm{e}}, z+1, g) \qquad [2.10]$$

where X, S and α are the excitation, ionisation and radiative recombination coefficients respectively, with g representing the ground level. By substituting Equation 2.9 into 2.8, the observed intensity is then related to the population density $N_{\mathrm{p}}^{\mathrm{z}}$ by

$$I_{\mathrm{p,q}}^{\mathrm{z}} = \frac{g(\nu_{\mathrm{p,q}})}{4\pi} \int N_{\mathrm{eo}} N_{\mathrm{g}}^{\mathrm{z}} X(T_{\mathrm{e}}, g, p) h\nu_{\mathrm{p,q}} R_{\mathrm{p,q}} \,\mathrm{d}x \qquad [2.11]$$

where $R_{\mathrm{p,q}} = A_{\mathrm{p,q}} \Big/ \sum_{\mathrm{q<p}} A_{\mathrm{p,q}}$ is the branching ratio.

A common application of the corona model is to determine T_{e} by the ratio of line intensities. Lines are chosen so that the excitation coefficients are sufficiently different from each other and for this reason ionic to neutral ratios are preferred. For a homogeneous plasma and using Equation 2.11, this ratio is given by

$$\frac{I_{\mathrm{p,q}}^{\mathrm{z+1}}}{I_{\mathrm{k,l}}^{\mathrm{z}}} = \frac{g(\nu)_{\mathrm{p,q}}}{g(\nu)_{\mathrm{k,l}}} \frac{N_{\mathrm{g}}^{\mathrm{z+1}}}{N_{\mathrm{g}}^{\mathrm{z}}} \frac{X(T_{\mathrm{e}}, g, p)\nu_{\mathrm{p,q}}}{X(T_{\mathrm{e}}, g, k)\nu_{\mathrm{k,l}}} \frac{R_{\mathrm{p,q}}}{R_{\mathrm{k,l}}} \qquad [2.12]$$

The instrumental calibration factors can be cancelled out if the line wavelengths are close enough. Substituting $N_{\mathrm{g}}^{\mathrm{z+1}} / N_{\mathrm{g}}^{\mathrm{z}} = S / \alpha$ Equation 2.10 and known expressions for the coefficients X, S and α (McWhirter, 1965) into the above equation yields

$$\frac{I_{\mathrm{p,q}}^{\mathrm{z+1}}}{I_{\mathrm{k,l}}^{\mathrm{z}}} = C^* T_{\mathrm{e}}^{3/4} \exp\left(-\frac{E_{\mathrm{i}}^{\mathrm{z}} + E_{\mathrm{p}} - E_{\mathrm{k}}}{kT_{\mathrm{e}}} \right) \qquad [2.13]$$

with $C^* = (g_{p,q} / g_{k,l})C$. Here E_i^z is the neutral ($z = 0$) ionization potential, $E_{p,k}$ are energies of levels p and k (relative to the ground state) and C is a constant containing the spectroscopic information (Desai *et al.*, 1995). The constant C^* can be determined either by calculation (Desai *et al.*, 1995) (with known instrumental factors) or experimentally by calibrating this expression with, for example, T_e obtained from Langmuir probe measurements (Hope *et al.*, 1987; Desai *et al.*, 1995). In an extension of the line-ratio method, Samsonov and Goree (1999) used 2-D imaging to obtain temperature maps of a RF plasma. Further improvements to the line-ratio method, including using neutral line ratios, can be found in Boffard *et al.* (2004).

Collisional radiative model

At higher pressures and plasma densities, collisional de-excitation can compete with spontaneous emission. Under these conditions

$$\sum_{m<p} A(p, m) \leq N_{eo} X(T_e, q, p) \qquad [2.14]$$

and the corona model is invalid. Additionally, step-wise collision processes, transitions via neighbouring levels and metastable states are neglected in the model.

The collisional radiative model (CR) attempts to overcome some of these restrictions by considering: (i) ionisation by electron impact (from any bound level) balanced by three-body and radiative recombination and (ii) transitions between bound levels by electron collisions and radiative transitions to the lower levels. Due to its complexity, the CR model is not discussed in detail here and further information can be found in McWhirter (1965), Benoy *et al.* (1991), Bogaerts *et al.* (1998) and Kano *et al.* (2000). Various CR models have been developed for low pressure discharges (Vlček and Pelikán, 1989), atmospheric discharges (Vlček and Pelikán, 1990), inductively coupled plasmas (Vlček and Pelikán, 1991), microwave (Alves *et al.*, 1992) and magnetron plasmas (Trennepohl *et al.*, 1996; Debal *et al.*, 1998; Guimarães *et al.*, 1993). An important aspect of the CR model can be inferred from Equation 2.14 towards the higher levels. As $A(p,m)$ decreases and X increases (due to closer energy level spacing), there will be a level p* where the corona model becomes invalid even at low pressures. The population densities for levels higher than p* will be in approximate local thermodynamic equilibrium (LTE) with the lower energy free electrons. The densities of levels p and q (where $p > q$) are then determined by the Boltzmann relation:

$$\frac{N_p}{N_q} = \frac{\omega_p}{\omega_q} \exp\left(-\frac{(E_p - E_q)}{k_B T_{exe}} \right) \qquad [2.15]$$

where T_{exe} is the excitation temperature and ω_{q} is the statistical weight (i.e. the number of states in the qth level).

By using Equations 2.8, 2.15 and the absorption oscillator strength, defined by $f_{\text{p,q}} = (M_{\text{e}}c^3/8\pi^2 e^2 \nu^2_{\text{p,q}})(\omega_{\text{p}}/\omega_{\text{q}})A_{\text{p,q}}$, it can be shown that:

$$\frac{I_{\text{p,q}}\lambda^3_{\text{p,q}}}{f_{\text{p,q}}\omega_{\text{q}}} = \left(\frac{8\pi^2 e^2 h}{M_{\text{e}}}\right)\frac{N_{\text{q}}}{\omega_{\text{q}}}\mathrm{e}^{-\frac{\mathrm{E_p}-\mathrm{E_q}}{\mathrm{k_B T_{exe}}}} \tag{2.16}$$

Also, by considering transitions that fall onto the same level q and taking logarithms, the above equation reduces to:

$$\ln\left(\frac{I_{\text{p,q}}\lambda^3_{\text{p,q}}}{f_{\text{p,q}}\omega_{\text{q}}}\right) = \ln\left(\frac{8\pi^2 eh}{M_{\text{e}}}\frac{N_{\text{q}}}{\omega_{\text{q}}}\mathrm{e}^{-\frac{\mathrm{E_q}}{\mathrm{k_B T_{exe}}}}\right) - \frac{E_{\text{p}}}{k_{\text{B}}T_{\text{exe}}} \tag{2.17}$$

A plot of $\ln(I_{\text{p,q}}\lambda^3_{\text{p,q}}/f_{\text{p,q}}\omega_{\text{q}})$ against E_{p}, called a Boltzmann plot, then yields a straight line of gradient $-1/k_{\text{B}}T_{\text{exe}}$. Tabulated values for $\lambda_{\text{p,q}}$, $f_{\text{p,q}}$ and ω_{q} can then be used with the measured $I_{\text{p,q}}$ to determine the excitation temperature. Since the vibrational states in molecules also follow the Boltzmann distribution, this procedure can be also used to measure the vibrational temperature. In this case, the Einstein coefficient $A_{\text{p,q}}$ is replaced by the Frank–Condon factors for vibrational transitions (Iza and Hopwood, 2004). The Bolztmann plot can also be used to obtain the rotational temperature, which describes the population of rotational states in molecules; however, the procedure differs from above as the rotational states follow a modified Boltzmann distribution (Motret *et al.*, 2000; Iza and Hopwood, 2004).

2.5.2 Line broadening

Spectral line profiles do not have infinitesimal spectral width due to the emitter's interaction with the surrounding medium. The resulting broadening of the spectral lines, when combined with the appropriate theory, can be useful for plasma diagnostics. Pressure broadening results from interactions of the emitters with neighbouring neutral and ionised particles and generally depends on temperature and pressure. Interactions with neutral particles (resonant and Van der Waals broadening) are usually insignificant compared to charged particles (Stark broadening) if the fraction of ionised particles is $\geq$–10^{-4}. Instrumental broadening, due to the finite resolution of the spectrometer, can also contribute to the observed line shape. For atmospheric air plasmas with plasma densities $N_{\text{eo}} < 10^{21}\,\text{m}^{-3}$ Van der Waals broadening can be significant. Natural broadening, which results from interaction with electromagnetic fields causing energy levels to have a spread in energy, is usually negligible compared with the other broadening mechanisms. Line shapes arising from the different broadening mechanisms are either Gaussian (instrumental, Doppler) or Lorentzian (Stark, Van der Waals, resonance, natural). An observed profile which contains Gaussian and Lorentzian elements is called a Voigt profile. If some of these elements are known, either theoretically or experimentally, they can be de-convolved from the Voigt profile to reveal the underlying line shape. Finally, broadening due to re-absorption of lines is usually negligible in low temperature plasmas. In plasma diagnostics, Doppler and Stark broadening are often the most useful and only these will be considered here.

Doppler broadening

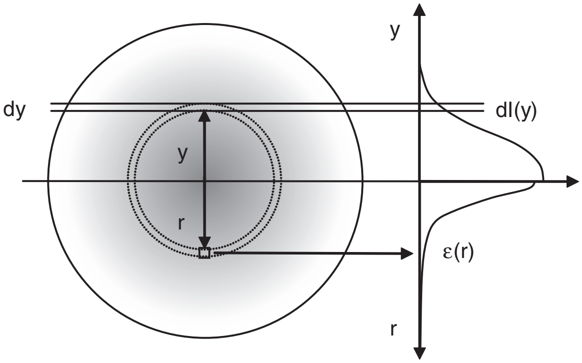
The motion of an emitter relative to an observer causes the wavelength λ to be shortened or lengthened, with the shift being proportional to its velocity. The combined Doppler shifts over a velocity distribution of emitters then give rise to line broadening. For a Maxwellian distribution, the peak's full width at half maximum (FWHM) is given by $\Delta\lambda_{1/2} = 7.16 \times 10^{-7}\lambda(T/M)^{1/2}$ where T is the temperature (in Kelvins) and M is the atomic weight (in a.m.u.). Thermal Doppler broadening is then most pronounced for the lighter elements, particularly for hydrogen. If the other broadening mechanisms, such as Stark broadening, can be neglected or accounted for, then measurements of the FWHM immediately give the emitter temperature. In pure hydrogen RF discharges, Doppler broadening of the H_α line (656.28 nm) can reveal features relating to dissociative excitation and ionisation by electron impact of H_2 and fast excited H neutrals (Radovanov *et al.*, 1995). The ionic mobility and plasma electric field can also be inferred from Doppler shifts by using velocity modulation laser spectroscopy (Radunsky and Saykally, 1988) or two-beam Doppler shift laser spectroscopy (Sassi and Daily, 1988).

Stark broadening

Stark broadening is the result of two mechanisms: (i) the combined shifting of spectral lines caused by the nearest neighbour electric fields of the slower positive ions and (ii) fast electron collisions that interrupt the otherwise unperturbed photon wave train. The shifting of spectral lines due to electric fields, called the Stark effect, is more pronounced for the higher energy levels. Under comparable conditions, some of the most strongly broadened lines are those of H, He^+, Ar^+ and O^+ in which the Stark shift is linear with electric field (linear Stark effect). For other elements the Stark effect is quadratic with electric field (quadratic Stark effect) and broadening is smaller. For hydrogen, the spectral shifts are symmetrical with no net shift whereas for other elements shifting as well as broadening is observed. The theory of Stark broadening is extremely complicated but approximate formulae can be derived that relate the line width to the plasma density for lines with weak temperature dependence. In this case the H_β (486.13 nm) Balmer line is particularly useful because good agreement between theory and experiment have been obtained, and the FWHM is related to the plasma density by the formulae $\Delta\lambda_{1/2} = 0.040N_{eo}^{2/3}$ nm where N_{eo} is in units of $10^{20}\,m^{-3}$. The temperature dependence of the H_γ (434.05 nm) line is more pronounced and Torres *et al.* (2006) exploited this, with measurements of the FWHM of both lines, to obtain the electron density and temperature from an atmospheric microwave discharge. In strong electric fields (~ kV/cm), Stark splitting of the H_α (656.28 nm) line can be used to measure the electric field strength. Wujec *et al.* (2003) applied this technique to a hydrogen dielectric barrier discharge at low pressure (~ kPa). In an atmospheric dielectric barrier discharge, Dong *et al.* (2005) used Stark broadening to obtain the micro-discharge electron density. In plasmas in which the Balmer lines are a convolution of Doppler-broadened and Stark-shifted profiles, electric fields can still be determined (Barbeau and Jolly, 1991).

2.5.3 Abel inversion

Abel inversion is a powerful method where line-of-sight intensity measurements can give information on the internal radial distribution of the plasma emissivity, $\varepsilon(r)$. This is defined as the radiant energy emitted from a volume dV per unit time into a solid angle dΩ. In general, emissivity is a function of position and direction and is closely related to intensity. The method is illustrated in Fig 2.11 in which a plasma slice is shown. Here $I(y)$ is the total intensity emitted by the plasma column of width dy at y, where distances



2.11 Schematic of a radially symmetric optically thin plasma. The observed intensity dI(y) is the total intensity from the plasma column of width dy. Integration of $[dI(y)/dy]\,(y^2 - r^2)^{-1/2}\,dy$ from y = r to the plasma edge (at y = 1) is related, by Abel inversion, to the radial emissivity ε(r).

are normalised to the plasma edge ($y = 1$). If the plasma is optically thin, has axial symmetry and $I(y = 1) = 0$ outside the plasma, then the intensity is related to the emissivity by Abel's inversion equation:

$$\varepsilon(r) = -\frac{1}{\pi}\int_{r=y}^{1} \frac{dI(y)}{dy}\frac{dy}{\left(y^2 - r^2\right)^{1/2}} \qquad [2.18]$$

The evaluation of this equation is not trivial since there are two main problems associated with the integral. Firstly, the derivative tends to amplify any inherent noise in the experimental data so that prior smoothing is necessary. Secondly, the integral exhibits a singularity at $y = r$ introducing significant errors at the start of integration. Errors can also occur when $dI(y)/dy \rightarrow 0$ at the axis of symmetry and at $y \approx 1$ (and are called termination errors). The evaluation of this integral using a direct approach usually yields unacceptable errors so more sophisticated techniques, such as polynomial fitting (Cremers and Birkebak, 1966), iteration (Vicharelli and Lapatovich, 1987), transform techniques (Smith and Keefer, 1988) and cubic splines (Gueron and Deutsch, 1994), are used.

2.6 References

Introduction

Becker K H, Kogelschatz U, Schoenbach K H and Barker R J (2005), *Non-equilibrium Air Plasma at Atmospheric Pressure*, Bristol, IOP Publishing.

Biederman H (2004), *Plasma Polymer Films*, London, Imperial College Press.

Hippler R, Pfau S, Schmidt M and Schoenbach K H (2000), *Low Temperature Plasma Physics*, Berlin, Wiley-VCH Verlag.

Hutchinson I H (1994), *Principles of Plasma Diagnostics*, Cambridge, Cambridge University Press.

Ovsyannikov A A and Zhukov M F (2000), *Plasma Diagnostics*, Cambridge, Cambridge International Science Publishing.

Discharge electrical characteristics

Bakker L P, Kroesen G M W and de Hoog F J (1999), 'RF discharge impedance measurements using a new method to determine the stray impedances', *IEEE Trans. Plasma Sci.*, **27**, 759–765.

Borcia G, Anderson C A and Brown N M D (2003), 'Dielectric barrier discharge for surface treatment: application to selected polymers in film and fibre form', *Plasma Sources Sci. Technol.*, **12**, 335–344.

Borcia G, Anderson C A and Brown N M D (2005), 'Using a nitrogen dielectric barrier discharge for surface treatment', *Plasma Sources Sci. Technol.*, **14**, 259–267.

Bose F, Patrick R and Baltes H P (1994), 'Characterization of plasma etch processes using measurements of discharge impedance', *J. Vac. Sci. Technol. B*, **12**, 2805–2809.

Braithwaite N St J (1997), 'Internal and external electrical diagnostics of RF plasmas', *Plasma Sources Sci.Technol.*, **6**, 133–139.

Dewan M N A, McNally P J, Perova T and Herbert P A F (2001), 'Use of plasma impedance monitoring for the determination of SF_6 reactive ion etch process end points in a SiO_2/Si system', *Mat. Res. Innov.*, **5**, 107–116.

Falkenstein Z and Coogan J J (1997), 'Microdischarge behaviour in the silent discharge of nitrogen–oxygen and water–air mixtures', *J. Phys. D: Appl. Phys.*, **30**, 817–825.

Hargis P J, Greenberg K E, Miller P A, Gerardo J B, Torczynski J R, Riley M E, Hebner G A, Roberts J R, Olthoff J K, Whetstone J R, Van Brunt R J, Sobolewski M A, Anderson H M, Splichal M P, Mock J L, Bletzinger P, Garscadden A, Gottschco R A, Selwyn G, Dalvie M, Heidenreich J E, Butterbaugh J W, Brake M L, Passow M L, Pender J, Lujan A, Elta M E, Graves D B, Sawin H H, Kushner M J, Verdeyen J T, Horwath R and Turner T R (1994), 'The Gaseous Electronics Conference Radiofrequency reference cell – A defined parallel-plate radiofrequency system for experimental and theoretical studies of plasma processing discharges', *Rev. Sci. Instrum.*, **65**, 140–154.

Lieberman M and Lichtenberg A (1994), *Principles of Plasma Discharges and Materials Processing*, New York, Wiley.

Sira M, Trunec D, Stahel P, Bursıkova V, Navratil Z and Bursık J (2005), 'Surface modification of polyethylene and polypropylene in atmospheric pressure glow discharge', *J. Phys. D: Appl. Phys.*, **38**, 621–627.

Sobolewski M A (1992), 'Electrical characterization of radiofrequency discharges in the gaseous electronics conference reference cell', *J. Vac. Sci.Technol. A*, **10**, 3550–3562.

Teuner D, Lücking C and Mentel J (1999), 'Electrical characterisation of capacitive RF discharges', *Proc. ICPIG XXIV*, **1**, 145.

Electrical plasma diagnostics

Aikawa H (1976), 'Measurement of anisotropy of electron-distribution function of a magnetized plasma', *J. Phys. Soc. Japan*, **40**, 1741–1749.

Alami J, Gudmundsson J T, Bohlmark J, Birch J and Helmersson U (2005), 'Plasma dynamics in a highly ionized pulsed magnetron discharge', *Plasma Sources Sci. Technol.*, **14**, 525–531.

Allen J E (1992a), 'Probe theory – the orbital motion approach', *Physica Scripta*, **45**, 497–503.

Allen J E (1992b), 'On the plotting of electron and ion distribution functions', *J. Phys. D: Appl. Phys.*, **25**, 1839–1840.

Allen J E, Boyd R L F and Reynolds P (1957), 'The collection of positive ions by a probe immersed in a plasma', *Proc. Phys. Soc. B*, **70**, 297–304.

Amemiya H (1986), 'Experiments on the energy-distribution function in hydrogen plasmas', *Jap. J. Appl. Phys.*, **25**, 595–600.

Amemiya H (1990), 'Plasmas with negative ions – probe measurements and charge equilibrium', *J. Phys. D: Appl. Phys.*, **23**, 999–1014.

Amemiya H and Yasuda N (1997), 'Capacitive radio frequency discharge plasma containing negative ions', *J. Phys. Soc. Japan*, **66**, 623–632.

Amemiya H, Annaratone B M and Allen J E (1999), 'The collection of positive ions by spherical and cylindrical probes in an electronegative plasma', *Plasma Sources Sci. Technol.*, **8**, 179–190.

Annaratone B M, Allen M W and Allen J E (1992), 'Ion currents to cylindrical Langmuir probes in RF plasmas', *J. Phys. D: Appl. Phys.*, **25**, 417–424.

Annaratone B M and Braithwaite N St J (1991), 'A comparison of a passive (filtered) and an active (driven) probe for RF plasma diagnostics', *Meas. Sci. Technol.*, **2**, 795–800.

Böhm C and Perrin J (1993), 'Retarding-field analyzer for measurements of ion energy distributions and secondary electron emission coefficients in low-pressure radio frequency discharges', *Rev. Sci. Instrum.*, **64**, 31–44.

Booth J P, Braithwaite N St J, Goodyear A and Barroy P (2000), 'Measurements of characteristic transients of planar electrostatic probes in cold plasmas', *Rev. Sci. Instrum.*, **71**, 2722–2727.

Boschi A and Magistrelli F (1963), 'Effect of an RF signal on the characteristic of a Langmuir probe', *Nuovo Cimento*, **29**, 487–499.

Bradley J W, Karkari S K and Vetushka A (2004), 'A study of the transient plasma potential in a pulsed bi-polar dc magnetron discharge', *Plasma Sources Sci. Technol.*, **13**, 189–198.

Braithwaite N St J and Allen J E (1988), 'Boundaries and probes in electronegative plasmas', *J. Phys. D: Appl. Phys.*, **21**, 1733–1737.

Bryant P, Dyson A and Allen J E (2001a), 'Langmuir probe measurements of weakly collisional electropositive RF discharge plasmas', *J. Phys. D: Appl. Phys.*, **34**, 1491–1498.

Bryant P, Dyson A and Allen J E (2001b), 'Langmuir probe measurements of weakly collisional electronegative RF discharge plasmas', *J. Phys. D: Appl. Phys.*, **34**, 95–104.

Bryant P (2003), 'Floating potential of spherical probes and dust grains in collisional plasmas', *J. Phys. D: Appl. Phys.*, **36**, 2859–2868.

Chabert P, Sheridan T E, Boswell R W and Perrin J (1999), 'Electrostatic probe measurement of the negative ion fraction in an SF_6 helicon discharge' *Plasma Sources Sci. Technol.*, **8**, 561–566.

Chatterton P A, Rees J A, Wu W L and Al-Assadi K (1991), 'A self-compensating Langmuir probe for use in rf (13.56 MHz) plasma systems', *Vacuum*, **42**, 489–493.

Chen F F (1965a), 'Electric probes', in Huddlestone R H and Leonard S L (eds), *Plasma Diagnostic Techniques*, New York, Academic Press, 113–200.

Chen F F (1965b), 'Numerical computations for ion probe characteristics in a collisionless plasma', *J. Nucl. Energy, Part C*, **7**, 47–67.

Chen F F (2001), 'Langmuir probe analysis for high density plasmas', *Phys. Plasmas*, **8**, 3029–3041.

Chou Y S, Talbot L and Willis D R (1966), 'Kinetic theory of a spherical electrostatic probe in a stationary plasma', *Phys. Fluids*, **9**, 2150–2167.

Chung P M, Talbot L and Touryan K J (1975), *Electric Probes in Stationary and Flowing Plasmas: Theory and Application*, New York, Springer.

Cohen I M (1963), 'Asymptotic theory of spherical electrostatic probes in a slightly ionized, collision-dominated gas', *Phys. Fluids*, **6**, 1492–1499.

Demidov V I, Ratynskaia S V and Rypdal K (2002), 'Electric probes for plasmas: The link between theory and instrument', *Rev. Sci. Instrum.*, **73**, 3409–3439.

DeNeef C P and Theiss A J (1979), 'Effect of finite analyzer size on the distribution functions measured in field-free plasmas', *Rev. Sci. Instrum.*, **50**, 378–381.

Donoso G and Martin P (1986), ‘Grid effects on velocity analyzers of variable geometry’, *Rev. Sci. Instrum.*, **57**, 1501–1506.

Donoso G and Martin P (1990), ‘Space-charge effects in a velocity analyzer of variable geometry’, *Rev. Sci. Instrum.*, **61**, 3381–3383.

Dyson A, Bryant P and Allen J E (2000), ‘Multiple harmonic compensation of Langmuir probes in rf discharges’, *Meas. Sci. Technol.*, **11**, 554–559.

Edelberg E A, Perry A, Benjamin N and Aydil E S (1999a), ‘Energy distribution of ions bombarding biased electrodes in high density plasma reactors’, *J. Vac. Sci. Technol. A*, **17**, 506–516.

Edelberg E A, Perry A, Benjamin N and Aydil E S (1999b), ‘Compact floating ion energy analyzer for measuring energy distributions of ions bombarding radio-frequency biased electrode surfaces’, *Rev. Sci. Instrum.*, **70**, 2689–2698.

Enloe C L and Shell J R (1992), ‘Optimizing the energy resolution of planar retarding potential analyzers’, *Rev. Sci. Instrum.*, **63**, 1788–1791.

Flender U and Wiesemann K (1994), ‘Ion distribution functions behind an rf sheath’, *J. Phys. D: Appl. Phys.*, **27**, 509–521.

Fujita F and Yamazaki H (1990), ‘Determination of electron energy distribution function of plasmas by digital processing from Langmuir probe characteristic’, *Jap. J. Appl. Phys.*, **29**, 2139–2144.

Godyak V A, Piejak R B and Alexandrovich B M (1992), ‘Measurements of electron energy distribution in low-pressure RF discharges’, *Plasma Sources Sci. Technol.*, **1**, 36–58.

Hershkowitz N (1989), ‘How Langmuir probes work’, in Auciello O and Flamm D L (eds), *Plasma Diagnostics*, Volume 1, New York, Academic Press, 113–183.

Honzawa T, Sekizawa T, Miyauchi Y and Nagasawa T (1993), ‘Effects of space charges in gridded energy analyzer’, *Jpn. J. Appl. Phys.*, **32**, 5748–5753.

Hopkins M B and Graham W G (1986), ‘Langmuir probe technique for plasma parameter measurement in a medium density discharge’, *Rev. Sci. Instrum.*, **57**, 2210–2217.

Ingram S G, Annaratone B M and Ohuchi M (1990), ‘Design and use of a gridded probe in a low-pressure rf argon discharge’, *Rev. Sci. Instrum.*, **61**, 1883–1891.

Ingram S G and Braithwaite N St J (1988), ‘Ion and electron energy analysis at a surface in an rf discharge’, *J. Phys. D: Appl. Phys.*, **21**, 1496–1503.

Iwama N, Lehner T, Noziri H and Okado M (1988), ‘Three-dimensional reconstruction of the ion velocity distribution function of plasma with a retarding-grid analyzer’, *Appl. Phys. Lett.*, **52**, 96–97.

Kamitsuma M, Chen S L and Chang J S (1977), ‘The theory of the instantaneous triple-probe method for direct-display of plasma parameters in low-density collisionless plasmas’, *J. Phys. D: Appl. Phys.*, **10**, 1065–1077.

Kamitsuma M and Teii S (1982), ‘Theory of a spheroidal probe in low-density continuum plasmas’, *Phys. Fluids*, **25**, 1169–1173.

Kennedy R V and Allen J E (2003), ‘The floating potential of spherical probes and dust grains. II: Orbital motion theory’, *J. Plasma Physics*, **69**, 485–506.

Kimura T, Yoneya A and Ohe K (1991), ‘Detection of electron energy distribution function by finite impulse response filter’, *Jap. J. Appl. Phys.*, **8**, 1877–1881.

Klagge S and Lunk A (1991), ‘Probe diagnostics of anisotropic plasma in a hollow cathode arc’, *J. Appl. Phys.*, **70**, 99–105.

Kono A (2003), 'Intrinsic sheath edge conditions for sheath instability in low-pressure electronegative plasmas', *J. Phys. D: Appl. Phys.*, **36**, 465–472.

Kortshagen U and Zethoff M (1995), 'Ion energy distribution functions in a planar inductively coupled rf discharge', *Plasma Sources Sci. Technol.*, **4**, 541–550.

Liu J, Huppert G L and Sawin H H (1990), 'Ion bombardment in rf plasmas', *J. Appl. Phys.*, **68**, 3916–3934.

Mezentsev A P, Mustafaev A S and Fedorov V L (1988), 'Probe measurements of the electron convective velocity in axisymmetric low-temperature helium plasmas', *J. Phys. D: Appl. Phys.*, **21**, 1464–1466.

Moskalev I N (1970), 'Influence of the first grid on the characteristics of a multigrid energy analyzer', *Sov. Phys. Tech. Phys.*, **15**, 371–376.

Niyogi K K and Cohen I M (1973), 'Continuum electrostatic probe theory with magnetic field', *Phys. Fluids*, **16**, 69–74.

Palop J I F, Ballesteros J, Colomer V and Hernández M A (1995), 'A new smoothing method for obtaining the electron energy distribution function in plasmas by the numerical differentiation of the I–V probe characteristic', *Rev. Sci. Instrum.*, **66**, 4625–4636.

Passoth E, Kudrna P, Csambal C, Behnke J F, Tichý M and Helbig V (1997), 'An experimental study of plasma density determination by a cylindrical Langmuir probe at different pressures and magnetic fields in a cylindrical magnetron discharge in heavy rare gases', *J. Phys. D: Appl. Phys.*, **30**, 1763–1777.

Piejak R B, Al-Kuzee J and Braithwaite N St J (2005), 'Hairpin resonator probe measurements in rf plasmas', *Plasma Sources Sci. Technol.*, **14**, 734–743.

Riemann K U (1991), 'The Bohm criterion and sheath formation', *J. Phys. D: Appl. Phys.*, **24**, 493–518.

Rubinstein J and Laframboise J G (1983), 'Theory of axially symmetric probes in a collisionless magnetoplasma: aligned spheroids, finite cylinders, and disks', *Phys. Fluids*, **26**, 3624–3627.

Sanmartin J R (1970), 'Theory of a probe in a strong magnetic field', *Phys. Fluids*, **13**, 103–116.

Sakai Y and Katsumata I (1985), 'An energy resolution formula of a three plane grid retarding field energy analyzer', *Jap. J. Appl. Phys.*, **24**, 337–341.

Schott L (1968), 'Electrical probes', in Lochte-Holtgreven W (ed.), *Plasma Diagnostics*, Amsterdam, North Holland Publishing Company, 668–731.

Self S A and Shih C H (1968), 'Theory and measurements for ion collection by a spherical probe in a collisional plasma', *Phys. Fluids*, **11**, 1532–1545.

Shih C H and Levi E (1971), 'The effect of collisions on cold ion collection by means of Langmuir probes', *AIAA J.*, **9**, 1673.

Simpson J A (1961), 'Design of retarding field energy analyzers', *Rev. Sci. Instrum.*, **32**, 1283–1293.

Sonmor L J and Laframboise J G (1991), 'Exact current to a spherical electrode in a collisionless, large-Debye-length magnetoplasma', *Phys. Fluids B*, **3**, 2472–2490.

Sowa M J, Blain M G, Jarecki R L and Stevens J E (2002), 'Spatially resolved electron temperature measurements with a microfabricated retarding field analyser', *Appl. Phys. Lett.*, **80**, 932–934.

Stangeby P C and Allen J E (1971), 'Transonic plasma flow past an obstacle', *J. Plasma Phys.*, **6**, Part 1, 19–32.

Stenzel R L, Gekelman W, Wild N, Urrutia J M and Whelan D (1983), 'Directional velocity analyzer for measuring electron distribution functions in plasmas', *Rev. Sci. Instrum.*, **54**, 1302–1310.

Su C H and Lam S H (1963), 'Continuum theory of spherical electrostatic probes', *Phys. Fluids*, **6**, 1479–1491.

Sudit I D and Woods R C (1994), 'A study of the accuracy of various Langmuir probe theories', *J. Appl. Phys.*, **76**, 4488–4498.

Swift J D and Schwar M J R (1970), *Electrical Probes for Plasma Diagnostics*, London, Iliffe.

Thompson S M and Bradley J W (2001), 'The effect of rotating cylindrical Langmuir probes in magnetron plasmas', *Contrib. Plasma Phys.*, **41**, 481–487.

Thompson B E, Allen K D, Richards A D and Sawin H H (1986), 'Ion bombardment energy distributions in radio-frequency glow-discharge systems', *J. Appl. Phys.*, **59**, 1890–1903.

Tichý M, Šícha M, David P and David T (1994), 'A collisional model of the positive ion collection by a cylindrical Langmuir probe', *Contrib. Plasma Phys.*, **34**, 59–68.

Welzel Th., Dunger Th., Kupfer H and Richter F (2004), 'A time-resolved Langmuir double-probe method for the investigation of pulsed magnetron discharges', *J. Appl. Phys.*, **96**, 6994–7001.

Woodworth J R, Abraham I C, Riley M E, Miller P A, Hamilton T W, Aragon B P, Shul R J, and Willison C G (2002), 'Ion energy distributions at rf-biased wafer surfaces', *J. Vac. Sci. Technol. A*, **20**, 873–886.

Plasma mass spectrometry

Barton D, Heason D J, Short R D and Bradley J W (2000), 'The measurement and control of the ion energy distribution function at a surface in an RF plasma', *Meas. Sci. Technol.*, **11**, 1726–1731.

Barton D, Short R D, Fraser S and Bradley J W (2003), 'The effect of ion energy upon plasma polymerization deposition rate for acrylic acid', *Chem. Commun.*, **3**, 348–349.

Biederman H (2004), *Plasma Polymer Films*, London, Imperial College Press.

Brink G O (1966), 'Electron bombardment molecular beam detector', *Rev. Sci. Istrum.*, **37**, 857–860.

Coburn J W and Kay E (1971), 'Pressure considerations associated with ion sampling from glow discharges', *J. Vac. Sci. Technol.*, **8**, 738–743.

Dawson P H (1976), *Quadrupole Mass Spectrometry and its Applications*, Oxford, Elsevier.

Haddow D B, France R M, Short R D, Bradley J W and Barton D (2000), 'A mass spectrometric and ion energy study of the continuous wave plasma polymerization of acrylic acid', *Langmuir*, **16**, 5654–5660.

Han L C M, Timmons R B, Lee W W, Chen Y Y and Hu Z B (1998), 'Pulsed plasma polymerization of pentafluorostyrene: synthesis of low dielectric constant films', *J. Appl. Phys.*, **84**, 439–444.

Hiden, http://www.hidenanalytical.com.

Howling A A, Sansonnens L, Dorier J L and Hollenstein Ch (1993a), 'Negative hydrogenated silicon ion clusters as particle precursors in rf silane plasma deposition', *J. Phys D: Appl. Phys.*, **26**, 1003–1006.

Howling A A, Dorier J L and Hollenstein Ch (1993b), 'Negative-ion mass-spectra and particulate formation in radio-frequency silane plasma deposition experiments', *Appl. Phys. Lett.*, **62**, 1341–1343.

Janes J and Börnig K (1993), 'Energy distributions of argon neutrals at the rf-powered electrode of a parallel-plate reactor', *J. Appl. Phys.*, **73**, 2724–2731.

Jarvis K E, Gray A L, Williams J G (1990), *Plasma Source Mass Spectrometry*, Cambridge, Royal Society of Chemistry.

Kae-Nune P, Perrin J, Guillon J and Jolly J (1995), 'Mass-spectrometry detection of radicals in SiH_4–CH_4–H_2 glow-discharge plasmas', *Plasma Sources Sci. Technol.*, **4**, 250–259.

Karkari S K, Bäcker H, Forder D and Bradley J W (2002), 'A technique for obtaining time- and energy-resolved mass spectroscopic measurements on pulsed plasmas', *Meas. Sci. Technol.*, **13**, 1431–1436.

Kawamura E, Vahedi V, Lieberman M A and Birdsall C K (1999), 'Ion energy distributions in rf sheaths; review, analysis and simulation', *Plasma Sources Sci. Technol.*, **8**, R45–R64.

Kusano E, Kobayashi T, Kashiwagi N, Saitoh T, Saiki S, Nanto H and Kinbara A (1999), 'Ion energy distribution in ionized dc sputtering measured by an energy-resolved mass spectrometer', *Vacuum*, **53**, 21–24.

Lieberman M and Lichtenberg A (1994), *Principles of Plasma Discharges and Materials Processing*, New York, Wiley.

Liu J, Huppert G L and Sawin H H (1990), 'Ion bombardment in rf plasmas', *J. Appl. Phys.*, **68**, 3916–3934.

McDowell C A (1963), 'Types of mass spectrometers', in Farmer J B (ed.), *Mass Spectrometry*, New York, McGraw-Hill, 7–44.

Mišina M, Bradley J W, Bäcker H, Aranda-Gonzalvo Y, Karkari S K and Forder D (2003), 'Investigation of the pulsed magnetron discharge by time- and energy-resolved mass spectrometry', *Vacuum*, **68**, 171–181.

Overzet L J, Beberman J H and Verdeyen J T (1989), 'Enhancement of the negative-ion flux to surfaces from radio-frequency processing discharges', *J. Appl. Phys.*, **66**, 1622–1631.

Pecher P and Jacob W (1998), 'Determination of the absolute CH_3 radical flux emanating from a methane electron cyclotron resonance plasma', *Appl. Phys. Letts.*, **73**, 31–33.

Rees J A, Seymour D L, Greenwood C L and Scott A (1998), 'An improved method for the study of neutral species produced in processing plasmas', *Nucl. Inst. Meth. Phys. Res. B*, **134**, 73–76.

Riemann K U (1989), 'Theoretical analysis of the electrode sheath in rf discharges', *J. Appl. Phys.*, **65**, 999–1004.

Robertson R and Gallagher A (1986), 'Monosilicon and disilicon radicals in silane and silane–argon dc discharges', *J. Appl. Phys.*, **59**, 3402–3411.

Sasaki S, Ishikawa I, Nagaseki K, Saito Y and Suganomata S (1997), 'Positive and negative ions in RF plasmas of SF_6/N_2 and SF_6/Ar mixtures in a planar diode', *Jap. J. Appl. Phys.*, **36**, 847–853.

Schwarzenbach W, Tserepi A, Derouard J and Sadeghi N (1997), 'Mass spectrometric detection of F atoms and CF_x radicals in CF_4 plasmas', *Jpn. J. Appl. Phys.*, **36**, 4644–4647.

Singh H, Coburn J W and Graves D B (1999), ‘Mass spectrometric detection of reactive neutral species: Beam-to-background ratio’, *J. Vac. Sci. Technol. A*, **17**, 2447–2455.

Stoffels E, Stoffels W W and Tachibana K (1998), ‘Electron attachment mass spectroscopy as a diagnostics for electronegative gases and plasmas’, *Rev Sci. Inst.*, **69**, 116–122.

Vlček J, Pajdarova A D and Musil J (2004), ‘Pulsed dc magnetron discharges and their utilization in plasma surface engineering’, *Cont. Plasma Phys.*, **44**, 426–436.

Vohrer U, Muller M and Oehr C (1998), ‘Glow-discharge treatment for the modification of textiles’, *Surf. Coat. Technol.*, **98**, 1128–1131.

Voronin S A, Alexander M R and Bradley J W (2005), ‘Time-resolved measurements of the ion energy distribution function in a pulsed discharge using a double gating technique’, *Meas. Sci. Technol.*, **16**, 2446–2452.

White F A and Wood G M (1986), ‘Types of Mass Spectrometers’, in *Mass Spectrometry Applications in Science and Engineering*, New York, Wiley, 51–88.

Zeuner M (2004), in Biederman H (ed.), *Plasma Polymer Films*, London, Imperial College Press, Chapter 4.

Zeuner M, Meichsner J and Rees J A (1996), ‘High energy negative ions in a radio-frequency discharge’, *J. Appl. Phys.*, **79**, 9379–9381.

Zeuner M, Neumann H, Zalman J and Biederman H (1988), ‘Sputter process diagnostics by negative ions’, *J. Appl. Phys.*, **83**, 5083–5086.

Optical emission spectroscopy

Alves L L, Gousset G and Ferreira C M (1992), ‘A collisional-radiative model for microwave discharges in helium at low and intermediate pressures’, *J. Phys. D: Appl. Phys.*, **25**, 1713–1732.

Barbeau C and Jolly J (1991), ‘Electric field measurement in the cathode sheath of a hydrogen glow discharge’, *Appl. Phys. Lett.*, **58**, 237–239.

Benoy D A, van der Mullen J A M, van der Sude B and Schram D C (1991), ‘A novel collisional radiative model with a numerical bottom and an analytical top’, *J. Quant. Spectrosc. Radiat. Transfer*, **46**, 195–210.

Boffard J B, Lin C C and DeJoseph Jr C A (2004), ‘Application of excitation cross sections to optical plasma diagnostics’, *J. Phys. D: Appl. Phys.*, **37**, R143–R161.

Bogaerts A, Gijbels R and Vlček J (1998), ‘Collisional-radiative model for an argon glow discharge’, *J. Appl. Phys.*, **84**, 121–136.

Chaivan P, Pasaja N, Boonyawan D, Suanpoot P and Vilaithong T (2005), ‘Low-temperature plasma treatment for hydrophobicity improvement of silk’, *Surf. Coat. Technol.*, **193**, 356–360.

Cooper J (1966), ‘Plasma spectroscopy’, *Rep. Prog. Phys.*, **29**, 35–130.

Cremers C J and Birkebak R C (1966), ‘Application of the Abel integral equation to spectrographic data’, *Appl. Opt.*, **5**, 1057–1064.

Debal F, Bretagne J, Jumet M, Wautelet M, Dauchot J P and Hecq M (1998), ‘Analysis of DC magnetron discharges in Ar-N_2 gas mixtures. Comparison of a collisional-radiative model with optical emission spectroscopy’, *Plasma Sources Sci. Technol.*, **7**, 219–229.

Desai T M, Gogawale S V, Shukla A B, Joshi N K, Salgaonkar U S and Bhale G L (1995), ‘Electron temperature measurements in uhv systems by spectroscopic and Langmuir probe techniques’, *Vacuum*, **46**, 223–226.

Dong L F, Ran J X and Mao Z G (2005), 'Direct measurement of electron density in microdischarge at atmospheric pressure by Stark broadening', *Appl. Phys. Lett.*, **86**, 1501–1503.

Donnelly V M (2004), 'Plasma electron temperatures and electron energy distributions measured by trace rare gases optical emission spectroscopy', *J. Phys. D: Appl. Phys.*, **37**, R217–R236.

Gueron S and Deutsch M (1994), 'A fast Abel inversion algorithm', *J. Appl. Phys.*, **75**, 4313–4318.

Guimarães F, Almeida J B and Bretagne J (1993), 'Study of an argon magnetron discharge used for molybdenum sputtering. II: spectroscopic analysis and comparison with the model', *Plasma Sources Sci. Technol.*, **2**, 138–144.

Hope D A O, Cox T I and Deshmukh V G I (1987), 'Langmuir probe and optical emission spectroscopic studies of Ar and O_2 plasmas', *Vacuum*, **37**, 275–277.

Iza F and Hopwood J A (2004), 'Rotational, vibrational, and excitation temperatures of a microwave-frequency microplasma', *IEEE Trans. Plasma Sci.*, **32**, 498–504.

Kano K, Suzuki M and Akatsuka H (2000), 'Spectroscopic measurement of electron temperature and density in argon plasmas based on collisional-radiative model', *Plasma Sources Sci. Technol.*, **9**, 314–322.

Laux C O, Spence T G, Kruger C H and Zare R N (2003), 'Optical diagnostics of atmospheric pressure air plasmas', *Plasma Sources Sci. Technol.*, **12**, 125–138.

Lochte-Holtgreven W (1968), 'Evaluation of plasma parameters', in Lochte-Holtgreven W (ed.), *Plasma Diagnostics*, Amsterdam, North Holland, 135–213.

McWhirter R W P (1965), 'Spectral Intensities', in Huddlestone R H and Leonard S L (eds), *Plasma Diagnostics Techniques*, New York, Academic Press, 201–264.

Motret O, Hibert C, Pellerin S and Pouvesle J M (2000), 'Rotational temperature measurements in atmospheric pulsed dielectric barrier discharge – gas temperature and molecular fraction effects', *J. Phys. D: Appl. Phys.*, **33**, 1493–1498.

Radovanov S B, Dzierżega K, Roberts J R and Olthoff J K (1995), 'Time-resolved Balmer-alpha emission from fast hydrogen atoms in low pressure, radio-frequency discharges in hydrogen', *Appl. Phys. Lett.*, **66**, 2637–2639.

Radunsky M B and Saykally R J (1988), 'Non-intrusive measurement of axial electric fields in low-pressure glow discharges by velocity modulation laser spectroscopy', *Chem. Phys. Lett.*, **152**, 419–423.

Raffaele A A, Riccardi C, Selli E, Barni R, Piselli M, Poletti G, Orsini F, Marcandalli B, Massafra M R and Meda L (2003), 'Characterization of plasma processing for polymers', *Surf. Coat. Technol.*, **174–175**, 886–890.

Richter J (1968), 'Radiation of hot gases', in Lochte-Holtgreven W (ed.), *Plasma Diagnostics*, Amsterdam, North Holland, 1–65.

Samsonov D and Goree J (1999), 'Line ratio imaging of a gas discharge', *IEEE Trans. Plasma Sci.*, **27**, 76–77.

Sassi M and Daily J W (1988), 'Doppler shift methods for plasma diagnostics', *J. Quant. Spectrosc. Radiat. Transfer*, **40**, 429–437.

Smith L M and Keefer D R (1988), 'Abel inversion using transform techniques', *J. Quant. Spectrosc. Radiat. Transfer*, **39**, 367–373.

Torres J, van de Sande M J, van der Mullen J J A M, Gamero A and Sola A (2006), 'Stark broadening for simultaneous diagnostics of the electron density and temperature in atmospheric microwave discharges', *Spectrochimica Acta Part B*, **61**, 58–68.

Traving G (1968), 'Interpretation of line broadening and line shift', in Lochte-Holtgreven W (ed.), *Plasma Diagnostics*, Amsterdam, North Holland, 66–134.

Trennepohl Jr W, Bretagne J, Gousset G, Pagnon D and Touzeau M (1996), 'Modelling of an Ar-O_2 reactive magnetron discharge used for deposition of chromium oxide', *Plasma Sources Sci. Technol.*, **5**, 607–621.

Vicharelli P A and Lapatovich W P (1987), 'Iterative method for computing the inverse Abel transform', *Appl. Phys. Lett.*, **50**, 557–559.

Vlček J and Pelikán V (1989), 'A collisional-radiative model applicable to argon discharges over a wide range of conditions. II: Application to low-pressure, hollow-cathode arc and low-pressure glow discharges', *J. Phys. D: Appl. Phys.*, **22**, 632–643.

Vlček J and Pelikán V (1990), 'A collisional-radiative model applicable to argon discharges over a wide range of conditions. III: Application to atmospheric and subatmospheric pressure arcs', *J. Phys. D: Appl. Phys.*, **23**, 526–532.

Vlček J and Pelikán V (1991), 'A collisional-radiative model applicable to argon discharges over a wide range of conditions. IV: Application to inductively coupled plasmas', *J. Phys. D: Appl. Phys.*, **24**, 309–317.

Wiese W L (1965), 'Line Broadening', in Huddlestone R H and Leonard S L (eds), *Plasma Diagnostics Techniques*, New York, Academic Press, 265–317.

Wujec T, Janus H W and Jeleński W (2003), 'Spectroscopic measurements of electric field distributions in dielectric barrier discharges in hydrogen', *J. Phys. D: Appl. Phys.*, **36**, 868–877.

3

Low-pressure cold plasma processing technology

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3.1 Introduction

Low-pressure cold plasma technology is also referred to as vacuum plasma technology. This technology has its origin in the processing of semiconductor materials and printed circuit boards (PCB). Examples of applications in these industries are the cleaning of lead frames before die attach or wire ball bonding, desmearing of printed circuit boards and the cleaning of vias for carbon removal after laser drilling (Fierro and Getty, 2003). The very fact that this technology started in these specific industries – which are generally considered as high tech – has been both a blessing and a curse. Although other industries, such as the automotive and medical device sectors (Vanlandeghem, 1994; Greger, 2002), adopted vacuum plasma technology in the 1980s, soon after its introduction in the electronics industry, the path to incorporation into the textile and nonwoven sectors has been and remains troublesome.

It is the everyday experience of the author that much of the reservation of the textile industry is due to fear for an (for them at least) unfamiliar technology, which is again based on a lack of information. This book in general and this chapter in particular is one of many attempts to help the textile industry to overcome this fear.

The present chapter, after a description of the basics of the technology, the potential effects that can be generated by it and the industrial equipment that is used, will concentrate on industrial applications of low-pressure vacuum plasma technology, mainly in the technical textile and nonwoven market segments. It is stressed that, for most of these applications, industrial size equipment is in usage for manufacturing purposes already. A few applications will also be discussed that are closer to 'classical textile'.

The driving forces for using vacuum plasma technology in the textile industry are similar to those found in other industries. In the general plastics industry for applications in automotive products and home appliances, the drivers were ecological, aesthetical and economical (Palmers, 2002). Since the early 1990s, there has been a definite trend to replace plastics such as polyvinylchloride (PVC) and acrylonitrile–butadiene–styrene (ABS) resin by polypropylene (PP) for reasons of recyclability. PP has, however, a much lower surface energy, typically 30 mN/m or less compared to PVC or ABS. It is hence more difficult to glue, or bond or paint. In addition, product designers needed to have more design freedom, forced by the end customers who want to individualise the products that they buy. In the case of rigid plastics, designers were not happy any longer with bulk coloured products (master batches), but wanted to have the freedom to paint their designs in all kinds of colour patterns and grades. Combine both major trends: PP and painting, and the market was stuck with a technological problem that is difficult to overcome with classical technologies. Indeed, there exist primers for PP; however, those are extremely expensive and in most cases not environmentally friendly. Low-pressure vacuum plasma technology has been able to solve this challenge in a successful way.

Therefore, also in the textile industry, one has to look for applications which lead to unique products in a cost-effective and environmentally sound way. Several examples of unique nonwoven products will be discussed in this chapter. They are, in most cases, based upon plasma-coated substrates using plasma polymerisation, a technology which came only in broad usage in 1995.

3.2 Low-pressure vacuum plasma technology

3.2.1 Generalities

The plasma state of a gas – also considered as the fourth aggregation state of matter – can be reached if the gas is under sufficiently low-pressure and when electromagnetic energy is provided to the gas volume. Under those circumstances, the process gas will be partially decomposed into radicals and atoms and will also be partially ionised. Depending on the frequency of the electromagnetic energy, the pressure range in which an equilibrium with a high density of charged particles is reached might be different. For the radiofrequency range (typically 40 kHz or 13.56 MHz), normally the working gas pressure is kept in the lower 0.1 mbar range, whereas for microwave sources, a working pressure between 0.5 and 1 mbar is often used. In order to effect the plasma treatment in sufficiently pure process gas conditions, a base pressure in the lower 0.01 mbar needs to be reached. This can be done with two-stage roughing vacuum pumps (rotary vane type) or with a dry pump or with a combination of either of those pumps with a roots blower.

Yet, different kinds of plasma modes are possible depending on whether only radicals and/or gas atoms are used or whether charged particles are also allowed to impinge on the substrate. The first mode is often given with terms such as chemical plasma, or soft plasma, or secondary plasma, or afterglow. The second mode is described as physical plasma, or hard plasma, or primary plasma. The difference between both is related to the mechanical/geometrical configuration of the plasma chamber. The plasma mode is chosen based on the exact effect that one wants to achieve and is also substrate-type dependent.

A plasma can bring several effects to substrates, depending on the plasma mode and the process gases used. There are five major effects of which three will be described in detail in the next sections: fine cleaning, *surface activation*, *etching*, cross-linking and *coating deposition*.

3.2.2 Surface activation by plasma

Surface activation by plasma is also referred to as chemical grafting (Terlingen, 1993). It never occurs alone, but always occurs during/after a plasma cleaning. Indeed, in the case of a substrate subjected to a soft secondary plasma which contains reactive species (e.g. oxygen atoms), the effect of those atoms will be twofold: they will react with organic contamination which is present on the substrate surface. Such organic contamination consists, in many cases, of loosely bound hydrocarbons. Both H and C will react with oxygen and will leave the substrate surface in the form of volatile H_2O and CO_2. Once the surface molecules of a polymer are freed from contamination, they can react with the oxygen atoms which will form carbonyl-, carboxyl- or hydroxyl functional groups on the substrate surface. It is said that the polymer surface has been chemically functionalised.

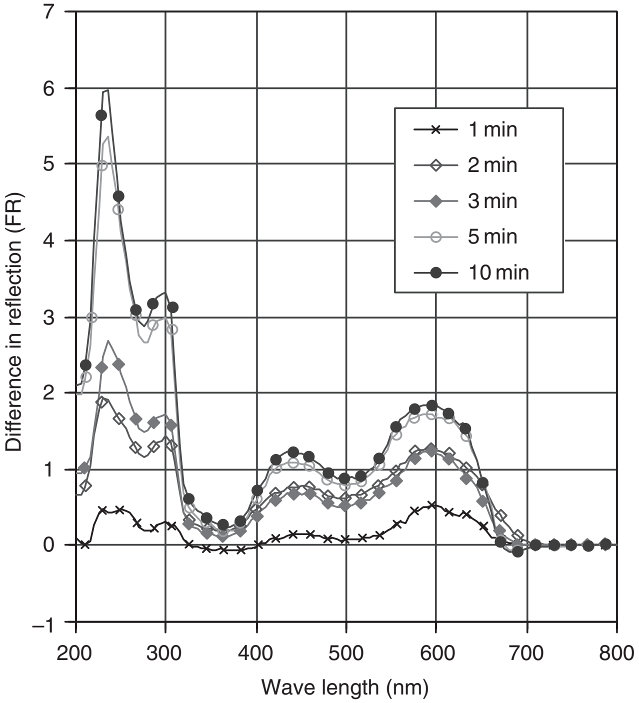
The effect of grafting carbonyl-groups onto a surface of PP, polyethylene (PE), or polyesters such as polyethyleneterephthalate (PET) or polybutyleneterephthalate (PBT) gives rise to an increase in surface energy to levels higher than 68 mN/m immediately after the plasma treatment. This effect is, however, not permanent: it has a certain shelf-life. Once the substrate has been removed from the plasma, and depending on the storage conditions, oxygen atoms will be released again from the surface molecules. This will happen slowly over time. After several days or even several months, the original surface energy of the substrate will have returned. The rate at which this happens depends on the type of substrate: e.g. PP has a fairly good shelf-life of a couple of weeks, whereas silicones show a shelf-life of less than one day. It further depends on the plasma conditions: an intensive plasma treatment will create a higher surface density of functional groups and, as such, the shelf-life will be longer.

Plasma activation is being used in several fabric and nonwoven applications in the textile industry. Section 3.4 gives some examples of such processes.

3.2.3 Etching by plasma

In order to perform an efficient etching process, a direct plasma is normally needed. In such a configuration, the substrate is bombarded with charged particles (ions and electrons) and apart from a purely chemical effect, the substrate is subjected also to a physical sputtering effect.

In the case of textiles and nonwovens, this effect of plasma treatment is not often used and hence we will not further elaborate on this later in the chapter. However, there is a certain potential even for fabrics. The textile market is trying to make deep, dark colours and this is not easy to achieve. One way to do this is to reduce the specular component of reflection of the fabric surface after dyeing. A plasma etching leads to a controlled nano- or micro-roughness, increasing diffuse reflectance and minimising the specular component. In consequence, the dyed fabric will have an intenser darker colour after plasma etching. As an example, for micro-PET fabric, colour depth increase ΔL is typically equal to 2.3. Figure 3.1 gives an example of



3.1 Difference in reflectance of several plasma-treated PET fabrics compared to untreated PET fabric. The curves are for plasma treatments with different dwell times: the longer the fibres are exposed to the plasma, the more pronounced the reflection difference is. (Results obtained by Europlasma N.V. in collaboration with the University of Ghent, Textiles Institute, Belgium, IWT-project 030471, Plasma-Colour.)

the reflection increase after different residence times in an etching plasma for micro-PET fabric.

Etching requires the removal of several hundreds of nanometres and etching processes are therefore slow. Needless to say, this technique is only viable for very high-end textiles.

3.2.4 Thin film deposition by plasma polymerisation

A very important usage of low-pressure vacuum plasma technology is thin film coating deposition by plasma polymerisation. In this specific case, reactive precursor gases that can polymerise are being used as process gases (Yasuda, 1976). The precursor gases are broken into radicals that react with each other on the substrate surface. The nature of the precursor gases will very much determine the properties of the deposited coating. Coating thickness is normally in the 10–50 nm range (5–30 molecular layers).

The very first applications of plasma polymerisation were found in the medical device industry. Micro-titre-plates are diagnostic devices normally made from polystyrene (PS); they consist of tiny cavities in which cell cultures are grown. A permanently hydrophilic coating on PS micro-titre plates gives rise to an improved culture growth on the plate.

There are many industrial applications of thin film deposition by plasma polymerisation in the technical textile and nonwoven industry. Roughly, the coatings deposited in those industries can be categorised under either (permanently) hydrophilic coatings or hydrophobic/oleophobic coatings. In most cases, the deposited coatings give rise to unique products that are difficult or even impossible to produce using other technologies. Section 3.5 discusses a number of those applications.

3.3 Equipment for low-pressure vacuum plasma technology

3.3.1 Web treatment equipment based on box-type vacuum chambers

Any plasma equipment has the following basic set-up. It consists of a vacuum chamber and a pumping group to evacuate this vessel. Of course, between the pumping group and the vacuum chamber, there are valves to isolate the pumping group from the chamber. Further, there are a set of mass flow controllers and valves in order to admit the process gases in a controlled way. In the chamber, there is an electrode system which is powered by one or more electromagnetic generators. Finally, there are several measurement aggregates such as pressure measurement gauges, thermocouples, etc. The entire equipment might be controlled by a micro-controller (programmed logic controller, PLC) or by a personal computer (PC). It is a basic characteristic of vacuum plasma systems that they are batch systems. The textile industry sees this very often as a limitation of the technology. They bring the argument that the rest of their production is in a continuous line and that they want to do the plasma treatment in line with other treatments on their webs. There are, however, four objections to this vision. First of all, even if many single operations in the textile industry are indeed continuous operations (reel to reel), the total process flow from either yarn or half-product fabric to finished fabric consists of several discrete (batch type) operations. The second objection has to do with process speed compatibility between various processes. Indeed, in most cases it will be difficult to tune the design of a plasma processing machine so that the web speed in that machine is under all circumstances equal to the web speed required for other processes before and/or after the plasma treatment. Thirdly, there is the overall process reliability argument. Contrary to many wet-processing machines, vacuum plasma machines are highly reliable and hence, once a process run is started, it does not often happen that the run needs to be interrupted. If several processes, including a plasma treatment, are being combined in line, then the probability of a breakdown on the whole line increases. Vacuum plasma equipment is indeed capital intensive equipment (as will be the case with most other equipment in the line) and a down time of such equipment because of problems with other processes will weigh on the overall profitability of the equipment. And finally, as Section 3.3.2 will show, roll-to-roll plasma treatment equipment allows the loading of considerable lengths of fabric or nonwoven (several thousands of linear meters), reducing the dead time for loading/unloading, pumping and venting to less than 5% of total available time.

Even using vacuum plasma technology, it is possible to build continuous air-to-air systems. Such systems have been built for the polymer film industry, but also recently for nonwovens. In such systems, both the unwind and rewind are located outside the vacuum, and the unwound web is fed through a series of load locks into the plasma processing zone of the equipment. Whereas the latter zone has a base pressure in the 0.01 mbar range, the series of locks has decreasing pressure going from the unwind to the processing zone. An identical series of load locks is mounted between the processing zone and the rewind of the equipment. On such a line, web coming from another equipment can be fed into the load locks directly. However, due to the many pumps, vacuum valves, pressure measurement gauges and complicated mechanics, the cost of such air-to-air vacuum plasma systems is considerable. Furthermore, it is a viable option only for thin nonwovens and not for thicker fabrics. Therefore, our general experience is that the textile industry should accept roll-to-roll batch plasma systems.

3.2 Vacuum plasma chamber with a classical loading system consisting of a set of trays.

Plasma systems can have all kinds of shapes and differ mostly in the loading system. Such a loading system might be a set of trays in which rigid parts are organised (see Fig. 3.2) or it might be a complete winding system for goods that can be wound, such as fabrics, nonwovens or foils. For smaller width webs, simple winding systems with a rewind motor and an unwind brake can be provided as a cassette that is mounted in a classical box-shaped vacuum chamber. Figure 3.3 shows an example of such a system. Of course, many variations to this basic design are possible including high-end winding systems with tension control and edge tracking.

3.3.2 True roll-to-roll web treatment equipment

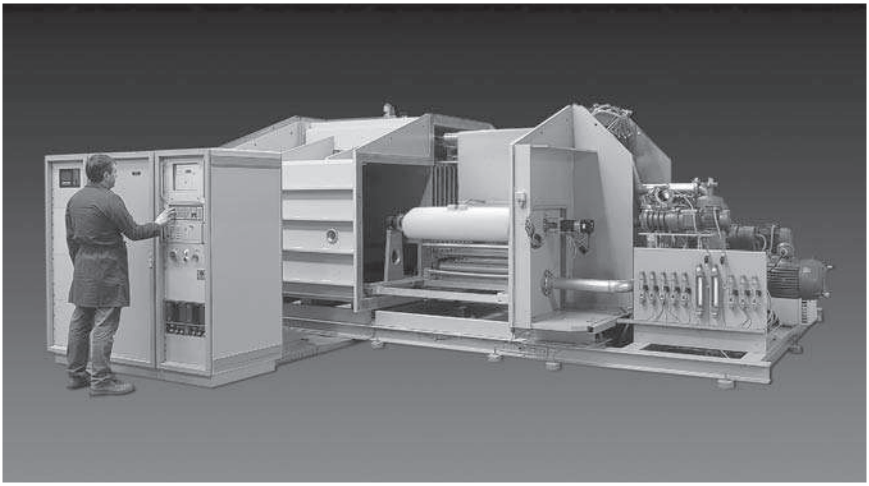
For vacuum plasma treatment of larger width webs (typically >0.6 m) starting from larger rolls (typically >0.3 m diameter), more complicated dedicated vacuum chambers are being built (Palmers, 2000a and b). Such chambers have normally three sections: an unwind, a rewind and a plasma treatment section, which might be differentially pumped. Typical web widths vary between 1.0 m and 3.2 m; maximum roll diameter is between 0.6 and 1.2 m. The rolls are normally provided on 75 mm plastic cores.

It is clear that the winding system of this type of equipment is much more complicated than the one from roll cassettes mentioned previously. All true roll-to-roll plasma treatment systems use tension control of the web. The web tension is measured by several load cells in the equipment and is fed

3.3 Roll cassette for the plasma treatment of small width webs in a classical box-shaped vacuum plasma system.

back to a number of capstans in the machine. This allows treatment of difficult-to-handle substrates, such as thin nonwovens, without too much stress on the web. The winding system in the plasma section consists of two rows of rolls at the bottom and top of the machine, respectively, so that the web is guided like a serpent through the plasma zone exposing as long a length of web as possible to the plasma. The plasma itself is generated with several electrode pairs, which are placed between various textile sections on the winding gear.

Figure 3.4 shows a typical industrial roll-to-roll vacuum plasma treatment machine for nonwovens. The processing sequence of substrate rolls in such equipment is as follows. With the vacuum chamber open, a new roll of substrate is loaded at the unwind side. The new roll is spliced manually to the remaining web of the previous roll. Then the web is inched manually through until the entire web is under constant tension. Now the vacuum chamber is closed and the chamber is evacuated with the vacuum pumps. When the base pressure is reached, process gas is entered into the vacuum chamber and left to stabilise. At the same time, the web is started moving. Now the plasma generator(s) is (are) turned on and the plasma is lit. The entire roll will be wound to the rewind side at a constant web speed during which it will be plasma treated. Once the vacuum chamber has been closed, the



3.4 Large industrial roll-to-roll vacuum plasma treatment machine (web width 1.8 m).

entire processing sequence runs automatically, controlled with a computer programme. During processing, no operator is needed. When the entire roll is at the rewind side, the generators are switched off, the process gas flow is stopped and the chamber can be vented. After opening the chamber, the treated roll can be removed from the rewind side.

Textiles and nonwovens, natural fibre materials and polymers alike, contain large quantities of water. This water will evaporate in the vacuum chamber during unwinding. Unfortunately, classical mechanical vacuum pumps do not effectively pump water vapour. Therefore, a Meissner trap (cryogenic coil) in the vacuum chamber is often installed.

Web speed in a roll-to-roll low-pressure vacuum plasma machine depends on three factors: type of required plasma effect (activation vs. coating), the required shelf-life or coating thickness respectively and the overall size of the plasma section in the machine (number of electrodes). For activation types of processes, a typical web speed is between 5 and 50 m/min. For coating deposition types of processes, the speed is between 0.5 and 10 m/min.

3.4 Plasma activation in the technical textile and nonwoven industries

3.4.1 Fabrics for automotive and medical applications

Some products in the automotive and medical applications industrial markets consist of a nylon (polyamide 66, PA66) fabric, which is coated with a silicone in a wet chemical process. Such fabrics are used in the automotive market to produce airbags. Similar fabrics are being used as supporting bandages.

For the airbag application, it is paramount to create a gas-tight fabric with as thin a silicone coating as possible. However, on nonplasma-treated PA66 rather thick coatings are required. If plasma activation is applied to the PA66 fabric prior to wet chemical coating, the nucleation of the latter is considerably improved, leading to a coating with lower porosity, which is already gas tight even for thinner coatings. As silicones are expensive materials, the plasma activation leads to considerable cost savings. In addition, there are other advantages: reduced weight of the airbag and less material usage (two generally important themes for the automotive industry).

In the case of medical support bandages, the requirement is also to reduce coating thickness, but it is also important that the silicone does not penetrate the entire thickness of the PA fabric. Due to the high affinity for silicones of the plasma-activated PA, rapid and high density nucleation of the coating takes place, so that the surface is quickly sealed off from further penetration of liquid silicone. For further examples see also Palmers, 2000a and b and Pane *et al.*, 2003.

3.4.2 Pre-treatment before dyeing

In various research programmes, it has been shown that pick-up of dyestuff can be strongly improved after plasma pre-treatment of natural fibre fabrics (woven or knitted cotton, linen, wool or silk). Contrary to this, for synthetic fibre fabrics, almost no improvement due to plasma pre-treatment is obtained. This is due to a different dyeing principle for synthetic fibre fabrics, i.e. dyeing is normally performed in a hot dye bath, the temperature increase causing opening of the fibre-structure to enclose the dyes. This limitation of improvement to natural fibres is, of course, a serious hindrance for commercial exploitation, the more so because it concerns products that are rather cheap per unit area of fabric.

As an example to show the potential of the technology, in a cooperation programme with IFP-research (Svensson, 2004), knitted fabrics of greige cotton were plasma treated and then dyed with various recipes. Dyeing was done by cold-pad-batch with reactive dyes from Ciba Specialty Chemicals (*Cibacron* of different colours). Whereas untreated reference samples showed a dyeing liquor pick up of 65–70% (depending on the dyeing recipe), the plasma treated samples were in the 80–89% range.

3.4.3 Activation of transportation textile before application of flame-retardant chemistry

Textiles used in transportation must receive a flame-retardant treatment. Currently, halogen-containing flame retardants are being banned for ecological reasons. The new kinds of flame-retardant chemistry, e.g. based on organic phosphonate derivatives, are much more expensive. Therefore, their usage should be limited to the absolute minimum.

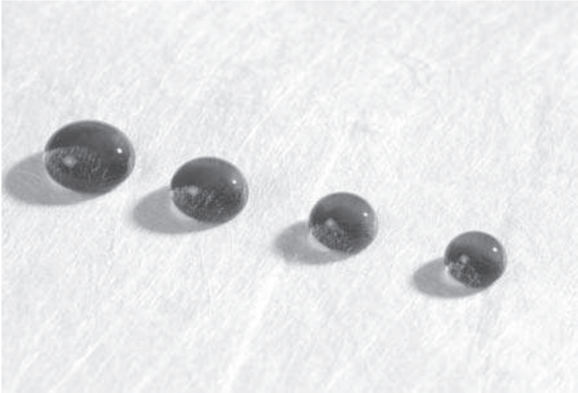
It has been shown that, in the case of plasma-activated fabrics consisting of both natural fibres and polymers, the concentration of flame-retardant chemicals can be reduced considerably without influencing the flame-retardant properties of the treated web. This again leads to considerable cost savings.

3.5 Plasma deposition on nonwoven materials

3.5.1 Hydrophobation of nonwovens for filtration applications

It is mainly plasma polymerisation for coating deposition that has found its way into the filtration industry. A first example of plasma coating can be found in air filter media both for respirator masks and for filters used in HVAC systems. Such filters consist of several layers of meltblown nonwoven PP, which are electrically charged (electrets). Filtration efficiency for oily particles can be greatly improved by applying a hydrophobic/oleophobic coating prior to electrical charging. Such coating is deposited starting from gaseous F-containing pre-cursors. Typical oil repellency grades of 3 to 4 using the 3M procedure (AATCC test method 118-1997) are achieved. Figure 3.5 illustrates this behaviour.

Table 3.1 gives an overview of filtration efficiency as measured with CERTITEST 8130 equipment using dioctyl phthalate (DOP) particles. Initial filtration efficiency and evolution of filtration efficiency can be



3.5 Water droplets on a plasma hydrophobated nonwoven PP, illustrating the water repellancy of the material.

Table 3.1 Filtration measurement results obtained by Europlasma in cooperation with a partner (proprietary) using a CERTITEST 8130 for different kinds of uncoated and plasma-coated filter media (5 layers)

Filter medium	Conditioning	Initial penetration (%)	Penetration after (x) minutes (%)
Supplier 1–28 g/m^2	Uncoated	1.20	6.40 (30)
Supplier 1–28 g/m^2	Plasma coated	0.48	1.08 (30)
Supplier 1–22 g/m^2	Uncoated	1.25	3.90 (10)
Supplier 1–22 g/m^2	Plasma coated	0.40	0.75 (10)
Supplier 2–25 g/m^2	Uncoated	N.A.	N.A.
Supplier 2–25 g/m^2	Plasma coated	0.02	0.03 (10)

measured. During measurement, the filter (consisting of five layers of single ply nonwoven PP) is loaded with 200 mg of DOP particles. Basically, the CERTITEST 8130 measures penetration (in %) over time and the efficiency (in %) is determined as 100% minus penetration. Penetration tests have been carried out on electrically charged filters.

Table 3.1 illustrates several effects of plasma coating on filtration efficiency. It is without doubt that a thin oleophobic plasma coating increases both initial and final filtration efficiency. In this sense, it can convert, e.g. an R95 filter into an R99 filter. However, a plasma coating cannot modify a Class III filter (which has decreasing filtration efficiency with time) into a Class II or Class I filter (constant or increasing filtration efficiency with time). For certain filtration materials, however, a plasma-coated filter medium shows excellent filtration efficiency, leading to a Class R100 filter! (See the Supplier 2 material in Table 3.2.)

Other applications of the same coating in the filtration industry have been developed. One example is the improvement of filtration efficiency of diesel filters based on nonwoven PBT.

This type of hydrophobic/oleophobic coating is not resistant to washing in hot (>80 °C) soapy water. In such an environment, the coating is gradually removed (complete removal after 3–4 wash cycles). This is what limits the usage of this coating in the classical garment textile industry. Filter media, however, are not subject to washing.

3.5.2 Hydrophilic coatings on nonwoven PP for battery separators

NiMhydride rechargeable batteries normally use a nonwoven meltblown PP separator web. The as-received substrate is hydrophobic. In order to improve wetting with the electrolyte, some manufacturers are using gamma rays to increase surface energy, but this is an expensive and even hazardous type of treatment. By applying a permanently hydrophilic type of coating out of gaseous pre-cursors, one can increase wetting behaviour of the battery separator considerably. Figure 3.6 illustrates this for a nonwoven meltblown PP of 40 g/m^2.

The rate of absorption of an alkaline solution (30% of KOH in demineralised water) was evaluated in a wicking test on 40 mm by 200 mm samples. For a 1 min wicking of a plasma-coated material, values between 22 and 25 mm were obtained immediately after plasma coating, whereas the uncoated reference material gave 0 mm (no wicking at all). Commercial reference materials on the market, which were not plasma coated, showed wicking values of only 5 to 10 mm.

Those measurements were repeated 21 days after plasma coating, resulting in values of 17–21 mm, proving also the permanent character of the coating. Finally, long-term resistance to KOH solutions was tested as follows. The samples from the wicking test performed 21 days after plasma coating were immersed in a beaker with 30% KOH solution. The beaker was covered with aluminium foil and was then put in an oven at 70 °C for 7 full days. After this, the samples were rinsed in demineralised water and air dried. Then the wicking test was repeated, showing wicking values of 16–18 mm.

Wash resistance of permanently hydrophilic coatings is better than for hydrophobic/oleophobic coatings but is still limited to about 7 wash cycles. Again, in the battery separator application, this is not important.

3.6 The economics of vacuum plasma treatment for fabrics and nonwovens

Contrary to what is generally believed, low-pressure vacuum plasma treatment, especially in large roll-to-roll equipment, is a highly economical

3.6 Illustration of wettability of meltblown nonwoven PP, coated with a permanently hydrophilic coating.

Table 3.2 Coating cost calculation for hydrophobic/oleophobic coating onto nonwoven meltblown PP for filtration applications

Cost factor	Comment	Cost per roll (€)	Cost per m^2 (€)
Depreciation cost	Depreciation over 10 years	239.7	0.018
Maintenance cost	Labour + parts	13.7	0.001
Total fixed costs		253.4	0.019
Electricity cost	@ 0.10 €/kWh	141.3	0.010
Process gas cost	Cons. 1800 litres/roll	240.0	0.018
Labour cost	@ 35.0 €/hour	52.5	0.004
Total variable costs		433.8	0.032
Total costs		687.2	0.051

technology. A typical full costing for plasma activation is in the range of 0.01 to 0.02 €/m^2. For plasma coating, the costs are higher because the web speed in such systems is normally lower and process gases are more expensive.

Table 3.2 shows an example of cost calculation for the case of a hydrophobic/oleophobic coating onto nonwoven PP (filtration applications). The cost evaluation has been done for a plasma coater Europlasma CD1800/600 ROLL with a maximum web width of 1800 mm, an outer roll diameter of 0.6 m (on 75 mm plastic core). We assume that the process runs at 5 m/min in order to reach an oleophobicity grade 3 on the 3M scale. Under these conditions, total processing time for a roll with length 7500 m and width 1.8 m, is 27 hours (meltblown nonwoven is about 20–25 g/m^2). Also, it is assumed that the system is used 7 days a week in a three-shift system for a total of 47 weeks per year. Under these conditions, the yearly capacity of the system is a 292 rolls of 13 500 m^2 each or 3 942 000 m^2.

Table 3.2 clearly indicates that total coating cost is in the 5 € cents per m^2 range. Permanently hydrophilic coatings would even cost less (because the precursor gases are less expensive).

For the case discussed in Table 3.2, fixed costs represent about 37% of total costs. This is a rather high fraction of total costs, which will be still higher for activation types of treatments. Therefore, it is important that the equipment is well dimensioned and that its capacity is fully exploited. Vacuum plasma equipment is extremely durable, with a service life of typically 15–20 years. Hence, depreciation can be chosen over longer periods of time (if taxation rules allow). A very positive thing is that variable costs are rather limited. Operating this equipment does not entail high costs.

3.7 Conclusions

Vacuum gas plasma technology has found its way into the industrial textile and nonwoven industries. In certain applications, chemical functionalisation of the textile surface by grafting active groups is being used, leading to cheaper products or products with improved quality. In the majority of applications, however, products with unique properties can be produced using plasma polymerisation of gaseous precursors for thin film coating deposition. Examples of such products have been discussed in the filtration industry (respirator masks) and in the field of rechargeable batteries (battery separator for NiMhydride rechargeable batteries).

The widely established misunderstanding that vacuum plasma technology is an expensive technology has been made invalid by a concrete calculation example. For many applications in industrial textile, cost is in the one to few Eurocents per m^2 range and is hence more than acceptable.

Another objection of the classical textile industry (garments, interior decoration, . . .) against this technology – the fact that it is a batch operation – has been shown to be almost irrelevant when large roll-to-roll equipment is being used.

The author hopes that the general reluctance of the textile industry to accept the vacuum plasma technology, which is based on a lack of training and information, has hopefully been alleviated by this chapter.

3.8 References

Fierro L., Getty J. D., 'Plasma processes for PCB manufacturing', *On Board Technol.*, Nov. 2003, 32–39.

Greger R., 'Pre-treatment of plastics with low-pressure plasma prior to flocking', *Flock*, **28**, 107 (2002), 7.

Palmers J., 'Roll-to-roll plasma treater for textiles and film treatment', *Coating Magazine*, December 2000(a), 465.

Palmers J., 'Roll-to-roll plasma treater to improve bonding and modify surfaces', *Coating Magazine*, December 2000(b), 469.

Palmers J., 'Economical Alternative to Primers', *European Plastic Product Manufacturer*, April 2002, 51.

Pane S., Tedesco R., Palmers J., 'Acrylic fabrics treated with plasma for outdoor applications', *Unitex*, July 2003, 13–17.

Svensson E., 2004, *Plasmatech – European Network Programme* (internal report).

Terlingen J. G. A., *Introduction of Functional Groups at Polymer Surfaces by Glow Discharge Techniques*, University of Twente, Enschede, 1993.

Vanlandeghem A., 'Plasma-Umweltfreundliche Kunststoffbehandlung', *Coating Magazin* 04, April 1994, 127–128.

Yasuda H., *Journal of Macromolecular Science – Chemistry*, **A10**, 383 (1976).

4

Atmospheric-pressure cold plasma processing technology

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4.1 Introduction

Although the power of plasma surface engineering across vast areas of industrial manufacturing, from microelectronics to medical and from optics to packaging, is demonstrated daily, plasma in the textile industry has been cynically described as the technology where anything can happen . . . but never does. Research into the application of plasmas to textiles goes back to the 1960s but, despite the reporting of novel and potentially commercial effects, it is only in recent years that plasma processing systems have begun to emerge into textile manufacturing in the production of specialty/high value fabrics.

It is instructive to look at major criteria for the introduction of new technology into the textile market and to assess plasma processing against such criteria. They can be separated into qualifiers (must be satisfied by the new technology as a minimum) and winners (motivate take-up of the new technology by the industry). Here are 'qualifier' criteria for new textile technologies:

- Safety and handling – The new technology must be operated safely, predominantly needing only the existing skill set of the textile mills.
- Operating speed – Line speeds need to be as fast as or faster than existing technologies to avoid bottlenecks.
- Production flexibility – Fast switching between fabric types and effects must be available to allow for rapid adaptations in product and process.
- Investment – The technology should offer a return on investment in under five years and maintain or improve the profitability of the mill.
- Environmental – The technology should comply with existing legislation and improve compatibility with anticipated law.

'Winner' criteria for new technology in textiles can be characterised as:

- New effects – Properties and performances not achievable by traditional technologies enabling added value and market differentiation.
- Durability – Significantly exceeds the durability of effects delivered by current processing techniques, again adding value and distinction.
- Operating Costs – Costs should be substantially reduced relative to established manufacturing norms, facilitating competitive pricing and/or profitability improvements.
- Environmental – Sets new industry benchmark.

To date, the plasma surface engineering community has barely begun to persuade the textile industry that plasma as a new textile processing technology either qualifies or wins as a mainstream production tool. It is apparent, however, that this position has begun to change with the placement in recent years of small numbers of plasma systems for particularly nonwoven processing with textile manufacturers. It would appear that, at last, evidence is emerging to support a prediction that plasma processing will move into mainstream textile manufacturing within five years, thus motivating textile manufacturers seeking new ways of competing to begin to take plasma technology seriously.

Why has plasma historically failed to qualify and win, and what new developments are addressing the roadblocks? It is stating the obvious to say that textile manufacturing is about the processing of large volumes of materials at high throughput. We are not dealing here with 300 mm diameter silicon wafers moving through a system at 20 per hour. Yet, it is this simple reality that has generated some of the toughest problems for plasma providers in their attempts to apply plasma technology to the textile industry. Plasmas are, in this context, about surfaces. They change the properties of any surface with which they come into contact, but first they must contact the surface to effect the desired change. In textiles, that surface typically comprises a woven, nonwoven or knitted fabric, perhaps 2.4 m wide and 10 km long. Ideally, every fibre in that system needs to be accessed by the plasma and at a speed and throughput that is high enough to make commercial sense. In a conventional textile wet padding line this is easily achieved by simple immersion of the fabric. Unfortunately, matters are not nearly so simple in the plasma context. It is not possible to fill up a bath of plasma and plunge in the fabric; the laws of physics are against us.

For one thing, the plasma needs a constant supply of energy just to keep alive. If the energy source is withdrawn, plasma relaxes back, within fractions of a second, into the gas state, losing all of its power and properties. Coupling-in the power needed to sustain the plasma is highly non-trivial and imposes all sorts of constraints on the equipment designer in terms of system geometry, operator safety, ease of use, cost, etc. Another problem is that plasma is generated from gas and the composition of the gas is a major factor in determining the properties of the plasma and the characteristics of the process. Unlike liquid in a bath, however, gas generally does not stay put but is easily displaced from where it is needed and is easily mixed with other, unwanted gases, particularly ambient air. In both cases, the plasma and its process are drastically changed, invariably for the worse. Again, maintaining the correct gaseous environment is far harder than maintaining a liquid bath and imposes serious constraints on equipment design.

These are obvious points yet are requiring huge engineering effort on the part of plasma equipment manufacturers to surmount and to make plasma processing compatible with the geometry and dynamics of textile processing. In essence, what are the most basic needs of the textile industry for a processing technology to be viable simply in terms of manufacturability? It needs large substrate area processing capability, cool operation not far from room temperature or, at least, not far from 100°C, and high throughput. These basic needs are readily met by wet processing but how realistic are they from the plasma perspective?

4.2 Basic manufacturability needs from plasma technology

4.2.1 Cool processing

Firstly, let us consider temperature. The plasma state of matter covers a truly staggering range of densities and temperatures; far, far greater than the other three states of matter, solid, liquid and gas, combined. From the centre of the sun to inter-galactic space, across 32 orders of magnitude in density and 8 orders of magnitude in temperature, the same laws of physics govern the plasma state. Technological plasmas for surface modification occupy only a small part of this parameter space but still vary in temperature from room temperature to >10 000 K. It is the job of the plasma equipment designer to ensure that the textile material only sees temperatures within a narrow range between about 0 and 100°C, preferably not above ~50°C. To this end, it is useful to distinguish two broad thermodynamic plasma regimes commonly called ‘equilibrium’ or ‘thermal’ plasmas and ‘non-equilibrium’ or ‘non-thermal’ plasmas. As has been described elsewhere, plasmas are a partially ionised gas containing ions, free electrons and neutral species as their microscopic constituents. To strike a plasma, energy is coupled into a gas volume until the volume suddenly begins to glow. At that moment, the system has become a different state of matter and has changed from the gas state to the plasma state, obeying different laws of physics. The energy has ionised enough of the gaseous neutrals to create a sufficient density of charged ions and free electrons to enable them to see each other due to their electrostatic charge and act collectively. It is this ability of the microscopic constituents of plasma to see each other at a distance due to their electrostatic charge that accounts for the dramatic differences in behaviour between plasma and the other states of matter, solid, liquid and gas. In these latter states, the microscopic species are electrostatically neutral and cannot interact at a distance but must actually collide to influence each other. In plasma, the ions, free electrons and neutrals constitute separate microscopic populations, each with its own characteristic temperature. If the free electrons are hot while the ions and neutrals are close to room temperature, the plasma is non-equilibrium. If, however, all three populations are close in temperature, the plasma is a thermodynamic equilibrium discharge.

Thermal plasmas are hot, those used for industrial surface engineering generally operating in the range 1000 to 10 000 K. In surface engineering they take the form of arcs, sprays, flames and jets and are used by industry in, for example, welding, metallurgy, coating with refractory materials and waste vitrification. They are obviously of no interest to textile manufacturers.

Non-thermal plasmas, in contrast, tend to be cool. The free electrons are very hot indeed, with typical temperatures ranging from 10 000 to 50 000 K, but the rest of the system, the ions and neutrals, is at or near room temperature. Because the free electrons comprise much, much less than one millionth of the total mass of the system, they have negligible heat capacity so that the actual heat content of the plasma is low. However, those hot, high energy electrons are key to the power of plasma in its ability to change surfaces. They career madly around the plasma volume, colliding with the other microscopic components and generating a wealth of new microscopic species with chemical and physical energy. Thus, the plasma becomes a soup of dozens of different, highly energetic species which, if a fabric, yarn or fibre/filament is immersed therein, will bombard the material. These fluxes of active species impact fabric at individual fibre level, resulting in profound modification of the surfaces immersed in the plasma. Depending upon the detailed nature of the plasma, the material can be etched (removal of bulk material), cleaned (removal of contaminant), activated (enhancement of the surface energy) or coated (deposition of a functional thin film). It is this ability to decouple and separately control the temperature of, on the one hand, the ions and neutrals, and, on the other, that of the free electrons that delivers a combination, unique in technology, of tremendous processing power with cool operation that makes plasma surface engineering such an appealing and widely used industrial tool. In essence, non-thermal plasmas can do things that no other technology can do and/or at a low temperature no other technology can attain. Non-thermal plasmas are, thus, of potentially great interest to the textile industry.

4.2.2 Large substrate area processing

As has been observed previously, the textile industry needs to process large area substrates, generally in the form of quasi two-dimensional, flexible webs, metres in width and kilometres in length. By definition, this requires spatially extended plasmas and, unlike wet processing where a bath is readily prepared to practically any dimensions, major engineering effort is needed to deliver equipment platforms that can generate large volume plasmas suitable for robust industrial processing.

Technological plasmas for surface modification cover a wide range of pressure regimes from ultra-high vacuum to atmospheric pressure. The laws of plasma physics make it easier technologically to generate large volume plasmas at reduced pressure than at atmosphere. Experimental data plotting both free electron and neutral temperatures in plasmas as a function of pressure show that, as system pressure increases from high vacuum towards atmosphere, the electron temperature decreases while neutral temperature increases, until they merge. In other words, as pressure rises, the plasma moves from a cool non-thermal to a hot thermal discharge due to the increasing collision rate and, hence, energy exchange between electrons and neutrals. This is one of the reasons why partial vacuum plasma technology has advanced significantly faster than atmospheric-pressure plasma technology in terms of surface engineering capability and is the industry standard workhorse in the large majority of sectors in which plasma is a mainstream production tool, such as microelectronics. In addition, a closed system under vacuum more easily contains and controls both the extent and the composition of the critical gas atmosphere from which the plasma is generated, and hence, the process chemistry, than does a system at atmospheric pressure with its perimeter open to the ambient air.

For these reasons, low-pressure plasmas have been more attractive from the perspective of large volume generation than atmospheric pressure plasmas and have, until recently, undoubtedly led the development of plasmas for textile processing. What, of course, many in the textile industry never fail to point out is that vacuum plasmas are not compatible with continuous, on-line processing and can only be employed in batch mode. But is this truly important? In many applications, probably yes, but in many others, no, provided that the benefits of the technology are clear and sufficient added value is demonstrated. Additionally, vacuum equipment is expensive in both capital and running costs. Atmospheric-pressure plasma (APP) would appear to have a significant advantage here but the discerning buyer will be careful to ensure that he/she is comparing like with like in terms of all attributes of the respective equipments. Thus, an APP air corona system may cost 10% of a low pressure glow discharge plasma system but it is certain that the process offered by the low-pressure system will be more sophisticated and of higher intrinsic value than air corona activation. But again, activation may be what the user needs to meet the performance target and it is all down to a proper definition of the textile manufacturer's needs and objectives and a benchmarking of competing solutions against these.

Since the 1980s, atmospheric pressure plasmas have increasingly been the subject of scientific research which has resulted in new (or re-discovered, often from basic research into gas discharges carried out in the 1920s and 1930s) and improved methods of APP generation. This, in turn, has fed into technological development so that there are now several APP types or configurations that meet the basic manufacturability criteria for textile processing. These are discussed below.

Besides covering the width of the textile to be processed, a large volume or, effectively, large area plasma extended along the direction of travel of the moving web, whether by festooning through a plasma volume or otherwise, offers extended residence time in the plasma. This can make for higher line speeds or better processing, e.g. thicker coating, higher energy deposition per unit area (J/cm^2), and potentially offers commercial advantage to those designs offering the largest area plasmas.

Finally, the treatment must not only be applied across large areas but must be uniform across the whole extent of the textile surface. This means that the plasma must be spatially uniform or, at least, uniform in the lateral dimension across the direction of travel of the web so that every part of the web sees the same level of treatment. Edge effects and singularities must be eliminated, not an issue with wet processing but needing careful design in plasma systems.

4.2.3 High throughput

The textile manufacturer will, of course, not want a newly introduced plasma process to create a bottleneck in an existing line or become a rate-limiting step in a drive to increase line speeds. This motivates the manufacturer to scrutinise carefully the claims of plasma providers as to throughput capability and investigate beyond headline line-speed figures of X metres/minute.

It is stating the obvious that atmospheric-pressure plasmas have a major throughput advantage over low-pressure plasmas in that they can operate in open perimeter mode allowing continuous, on-line processing interfaced to a conventional production line, while vacuum plasma must operate off-line in batch mode. But this is by no means the whole story. The vacuum plasma run speed for the target process could be an order of magnitude faster than the APP line speed, which can wipe out the supposed APP advantage when a holistic view is taken of the plasma logistics. It is essential that all steps in the throughput process are individually assessed and integrated into an overall timing picture. Thus, loading/unloading of a vacuum system, roll transfer, pumpdown (often a strong function of the material being treated) and venting, downtime for chemical precursor reload, the compatibility of a treated fabric with being rewound onto itself before onward processing, i.e. the need for immediate post-plasma processing (more of a process than a throughput issue), etc. are examples of operations needing to be factored into a realistic throughput model. Nevertheless, it is fair to say that, all other things being equal, a rare enough occurrence, APP systems will probably have an edge over low pressure plasma in the matter of throughput.

4.2.4 Summary of the basic manufacturability needs

In summary, the bare minimum that the textile industry must have from plasma providers in terms of manufacturability is equipment platforms generating non-thermal plasma in a geometrical configuration suitable for uniform treatment of large area flexible web. These two simple sounding conditions drastically limit both the type of plasmas that can be used in textile manufacturing and the configurations in which they can be employed. Essentially, one plasma type is compatible with textiles in the low-pressure regime – the Glow Discharge, and three types are compatible at atmospheric pressure – the Corona, the Dielectric Barrier Discharge, the Atmospheric Pressure Glow Discharge.

In the current state of development of plasmas for textile manufacturing, there is no single ideal and clearly superior plasma technology for textile manufacturing. Atmospheric-pressure plasma is not intrinsically superior to low-pressure plasma or vice versa. It's 'horses for courses'. Each technique has different attributes and strengths and the prudent textile manufacturer will carefully define his/her objectives and needs and carry out a detailed assessment of the available equipment and process combination options and their fit to the defined product performance, manufacturability and financial criteria. In essence, everything depends on what the textile manufacturer wants to achieve with plasma technology. Is it to create a unique product with new effects and properties? If so, it is likely to be a high performance product aimed at the top end of the market commanding a premium price. Although small in terms of annual output (m^2 per year), high performance textiles are rapidly growing in economic importance and, due to their high value, can generate serious revenue at high margins from even small production batches. Examples are in filtration, medical and biotechnology. In such a case, the textile producer should look closely at the plasma world, firstly because this sort of niche, high-value opportunity is ideal for the introduction of new technology and, secondly, because plasmas have demonstrated many new and potentially commercial effects precisely in the high technology market segments which are offering these opportunities. In that case, the high investment cost of, say, a €1 million plasma system capable of sophisticated functional coatings with bio-compatibility, for example, may well be justified by fast returns. On the other hand, is the goal to reduce raw material costs or to eliminate increasingly expensive environmental costs associated with the use of water, power and chemicals disposal? Plasma appears to be an excellent candidate to achieve all of these. Thus, functionalisation of a fabric surface by coating with, for example, a fluorocarbon waterproofing consumes grams or tens of grams per m^2 of coating material in conventional wet finishing processes. Plasma can deposit the same effect with a 50 milligram per m^2 coating, saving raw material, waste and water consumption and using a small fraction of the energy. But, does the plasma coating fully meet the product performance needs, e.g. in terms of washability, and, since the aim is to reduce costs, how much can the textile company afford in terms of new capital cost and write-off of existing investment? In the drive to accurately model and predict the financial consequences of investment in plasma, the textile manufacturer should expect the plasma provider to deliver detailed and comprehensive capital and running cost data based upon established performance specifications for both equipment and process. Anything less is a leap in the dark.

While dealing with the issue of competing solutions, it must be said that the plasma community as a whole points to the potentially significant advantages over its major technological competitor, namely conventional wet and heat based processing. These points are particularly strong in the case of atmospheric pressure plasmas due to the ability of these to compete with wet processing on an equal basis in the sense of being fully compatible with continuous, in-line processing. Table 4.1 summarises the perceived advantages of plasma processing over wet processing, particularly with respect to APP.

4.3 Atmospheric-pressure plasma types for textile processing

As concluded previously, the constraints upon size and temperature applying to any technology seeking to process textiles limit the scope of plasma engineers in the search for new solutions that can generate value for textile manufacturers. It is useful to glance at some of the underlying physical principles that constrain the development of non-equilibrium atmospheric-pressure plasmas for this application. Three physical phenomena play a strong role in this APP development:

Table 4.1 Perceived advantages of plasma processing over wet processing, particularly with respect to APP

Manufacturing operation	Conventional Wet/heat processing	Plasma processing
Handling and storage of bulk chemicals	Yes	No
Mixing of chemicals, formulation of baths	Yes	No
Use of water	Heavy	None or very low
Raw materials consumption	High	Low
Drying ovens and curing operations	Yes	No
Need for solvents, surfactants, acids	Yes	No
Number of process steps	Multiple	Single
Energy consumption	High	Very low
Waste disposal/recycling needs	High	Negligible
Environmentally costly	Yes	No
Equipment footprint	Large	Small
Manufacturing versatility from single kit	Limited to single or few process options	Depending on kit, can be highly flexible with wide range of available processes
Innovation potential	Moderate	Very high

- The dependency of gas electrical breakdown on pressure
- The inverse scaling of the characteristic dimension of the plasma, i.e. its size, with pressure
- The glow-to-arc-transition.

4.3.1 The dependency of gas breakdown on pressure

To strike or ignite plasma from a volume of gas, the electrical breakdown voltage, V_b, of the gas must be exceeded. There are a variety of ways in which electromagnetic energy may be coupled into a gas volume to create the strong electric fields needed for gas breakdown but, for the purposes of textile processing, the relevant techniques all employ the same basic concept, namely a pair of opposing conductive electrodes (generally, but not always, constructed from metal) separated by a gap containing the gas from which the plasma is to be generated and across which is applied a voltage from an external power supply. The electrodes come in varied shapes and sizes, but for most configurations, mainly those not involving geometrical singularities such as sharp points or edges, a physical relationship called Paschen's Law applies relating V_b to the product of two system parameters, namely electrode spacing, d, and gas pressure, p. Thus, V_b is a function (generally not linear) of $(p.d)$:

$$V_b = f(p.d)$$

At the microscopic scale, Paschen's Law reflects a particular mode of gas breakdown called the Townsend breakdown mechanism in which neutral atoms/molecules are ionised by collision with an energetic free electron. Such an event generates a positive ion and another free electron. The two free electrons are then accelerated by the electric field, thus picking up energy, and when that energy exceeds the energy needed to knock a bound electron out of a neutral, the next free electron/neutral collision will generate yet another free electron. This process continues, resulting in a cascading of electrons generated by collisions in the inter-electrode gap until the density of charged species is high enough for the gas to change state and strike a plasma.

The technological consequence of Paschen's Law is that, for a fixed external applied voltage (generally determined by the parameters of the power supply and circuit), the inter-electrode spacing, d, must decrease as pressure rises towards atmospheric if a plasma is to be struck. So, whereas at low pressure the electrodes can be widely spaced, allowing generation of large volume plasmas, by the time the pressure has reached atmospheric, d is of the order of mm. Thus, for example, V_b for the gas argon, a technologically interesting gas for plasma textile processing, is about 2.5 kV at atmospheric pressure if the inter-electrode gap is 5 mm. The narrow gap needed at atmospheric pressure for gas breakdown at the reasonable applied voltages ~10 kV consistent with industrial operations is a major constraint on the geometry of APP systems since, for example, it makes it difficult or impossible to pass very thick fabrics through the plasma region for treatment. In practice, thin to medium thickness fabrics are fully treatable within the inter-electrode gap and very thick fabrics can be treated in what is called 'downstream' mode. Here, the plasma is generated in the narrow inter-electrode gap or in jet form, and is blown outside that region by gas flow directly onto the fabric, which can be of any thickness. The German company Plasmatreat GmbH[1] supplies a range of ingenious and highly robust plasma jet systems which can be configured in fixed or rotating arrays to ensure coverage of wide area textiles at good line speeds.

4.3.2 Inverse scaling of size with pressure

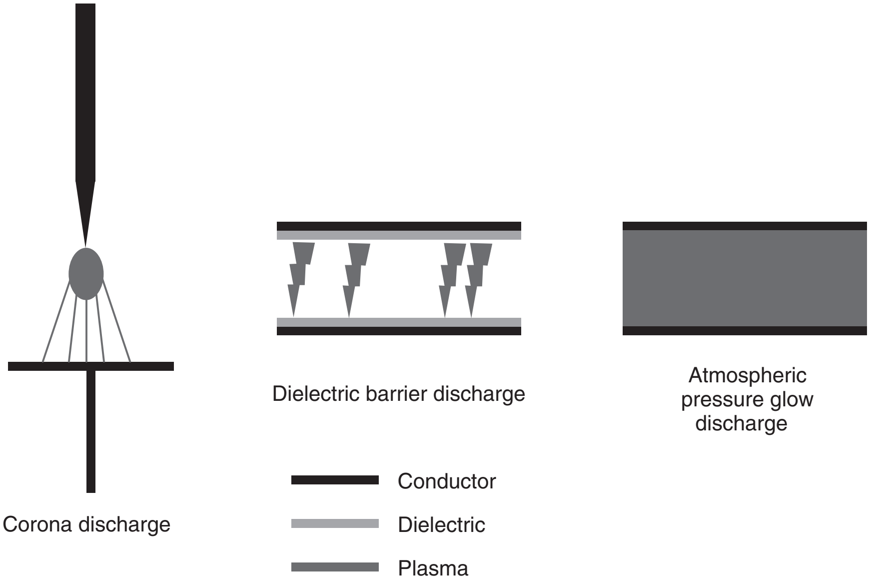
We have discussed the need for large plasmas so that it is an unfortunate fact of nature that plasmas at atmospheric pressure tend to want to be small.

In essence, as the pressure of the plasma system rises, the plasma shrinks in volume and shrinks quite rapidly. The relevant physical relation is:

$$J_n \propto p^2$$

where p = pressure (Pa) and J_n = current density (A/m^2) flowing through the electrical circuit incorporating the plasma and sustaining it with electromagnetic energy. For constant current, the physical relation states that the current density in the plasma increases with the square of the pressure. This means that, at constant current, the cross-sectional area of a glow discharge plasma generated at low pressure decreases with increasing pressure so that, while cross-sectional areas of plasma are, at low pressures, of the order of the dimensions of the electrodes used to generate the plasma (many cm^2), at atmospheric pressures, typical cross-sectional areas of that plasma have shrunk to a few mm^2, useless for textile processing.

The solution to this phenomenon has been for the plasma engineers to move away from the methods used to generate low-pressure plasmas and to find new techniques for APP generation that are not constrained by the above relation. The results have been the development of three types of APP that have relevance for textile treatment – the Corona Discharge, the Dielectric Barrier Discharge, the Atmospheric Pressure Glow Discharge. Figure 4.1 indicates their modes of generation.



4.1 Schematic of the modes of generation of the three APP types for textile treament.

The corona discharge

Corona discharges are plasmas that result from the high electric field that surrounds an electrically conductive spatial singularity when a voltage is applied. Corona generation systems usually take the form of two opposing electrically conductive electrodes separated by a gap containing the gas from which the plasma is generated and connected to a high voltage source. The geometry of the electrodes is highly asymmetric, examples being sharply pointed needle or thin wire electrodes opposing flat planes or large diameter cylinders. These are powered with high, continuous or pulsed d.c. or a.c. voltages. The high electric field around the singularity, i.e. the point of the needle or the wire, causes electrical breakdown and ionisation of whatever gas surrounds the singularity, and plasma is created, which discharges in a fountain-like spray out from the point or wire. Plasma types are characterised, *inter alia*, by the number, density and temperature of the free electrons in the system. Coronas are very weakly ionised with a free electron density of about 10^8 electrons/cm^3, which compares with the particle density of a gas at atmospheric pressure of ~10^{19} particles/cm^3. The corona is strongly non-thermal with some very high energy free electrons with temperatures in excess of 100 000 K. The wire configuration, in principle, can meet the need for large area processing by being stretched across the web orthogonal to the direction of travel and just above the fabric surface. However, the corona is spatially non-uniform with the plasma density dropping off rapidly with distance from the point of generation, requiring a small inter-electrode gap. The discharge is so narrow that the residence time of the fabric in the plasma would be too short for commercial operation and, in addition, the power level that can be applied is extremely limited by the cross-section capacity of the wire and its ability to dissipate heat generated during treatment. Accordingly, in its pure form, corona is far from an ideal textile surface processing medium.

The dielectric barrier discharge

In contrast to the asymmetry of the corona system, if a symmetrical electrode arrangement is set up comprising two parallel conducting plates placed in opposition, separated by a gap of ~10 mm, and a high voltage, 1–20 kV, is applied, the gas between the plates can be electrically broken down and a plasma discharge generated. Generally, however, that plasma takes the form of a hot thermal plasma arc less than a millimetre in diameter, which jumps from one spot on one electrode plate to a spot on the opposing electrode. This is useless for textile treatment and would do nothing except burn a hole in the fabric. If, however, one or both of the electrode plates is covered by a dielectric such as ceramic or glass, the plasma finds it much more difficult to discharge as an arc and, instead, is forced to spread itself out over the area of the electrodes to carry the current it needs to survive. This type of plasma is called a Dielectric Barrier Discharge (DBD) and is large area, non-thermal and uniform. Because of charge accumulation on the dielectric, which tends to neutralise the applied electric field thus choking off the plasma, the DBD must be powered by a.c. and is typically driven by high voltage power supplies running at frequencies of 1 to 100 kHz. It is denser than the corona with a typical free electron density of about 10^{10} electrons/cm^3 but the free electrons are slightly cooler at temperatures of 20 000 to 50 000 K. This is a much more attractive candidate for textile processing than the pure corona.

The DBD can take two forms, filamentary and homogeneous, the latter confusingly sometimes called, again, atmospheric-pressure glow discharge, although it will be referred to here as the homogeneous DBD. The most common form is filamentary, where the plasma appears as an array of discrete, tiny 'microdischarges'. These are parallel filamentary plasma current channels running directly between and normal to the electrodes. They are ~100 μm in cross-sectional diameter and carry a high current density of ~100 A/cm^2 but have a lifetime of only a few nanoseconds. The accumulation of local electrical charge on the dielectric at the foot of each microdischarge reverses the local electric field, thus locally neutralising the driving voltage, choking off the current flow and quenching the microplasma nanoseconds after it has fired. Although, in theory, the spatial distribution of the microdischarges should be random so that, integrated over time (generally less than a second), the entire volume between the electrodes should experience a microdischarge and thus visually appear as a continuum of plasma, i.e. a uniform, featureless glow, in practice imperfections, singularities and transients in the electrodes, the dielectric and the inter-electrode medium generate preferred plasma striking points. This is exacerbated by the tendency of plasma to strike at points on the electrode plane containing residual electric charge. The result is not a continuum of plasma but, to the eye looking sideways into the gap between electrodes, a series of bright, vertical plasma micro-columns some of which appear to move, some to remain fixed in an entrancing display of light and movement. In any event, because of the short duration and, thus, the limited charge transport and energy dissipation in each microdischarge, there is typically little gas heating (very much an unwanted phenomenon tending to generate the dreaded thermal plasma) so that a large portion of the free electron energy is utilised for exciting atoms or molecules in the background gas, thus creating the precursors needed to initiate surface chemical reactions and/or emission of radiation, which energetic photons can also help to drive surface chemistry. This explains the great interest in DBDs for many applications.

The homogeneous DBD mode relies upon the same basic electrode configuration. Through variation of control parameters such as the composition of the generation gas, the frequency of the applied power and the spacing of the electrodes, the filamentary DBD can be converted to a diffuse, continuous and homogeneous discharge that presents the appearance of a uniform glow throughout the plasma volume. To the eye, both the filamentary and the homogeneous DBD appear to be continuously discharging, despite their spatially distinct characteristics. In fact, both are pulsing on and off in time with the driving frequency of the applied power but at a rate far too fast for human vision to distinguish. The difference is that the filamentary plasma pulse is composed of the sum of multiple small, individual current micro-pulses per half cycle of driving frequency, reflecting its microdischarge nature, while the homogeneous DBD is characterised by only a single large current pulse per half cycle of driving frequency which current is not concentrated into tiny micro-streamers but is uniformly diffused throughout the entire inter-electrode volume, hence its homogeneous and spatially uniform nature.

The homogeneous DBD is certainly the preferred DBD mode from the textile processing perspective. By definition, it is spatially uniform and avoids the danger of pin-holing of fabric passing through the plasma. This can be caused by energetic microdischarges in the filamentary mode, as strong microdischarges can act like mini-arcs, vaporising fibres and burning pin-holes. The filamentary DBD plasma is, because of its structure, only in limited contact with the fabric at any instant in time, essentially in the small volume plasma channels of the microdischarges. This results in non-uniform treatment and low processing speeds in order to give the plasma a chance to contact more of the fabric. Furthermore, it is claimed that, although the filaments of the DBD can be a rich source of reactive species, the discharge produces a relatively low spatially average density of useful microscopic species because most of the active atoms and molecules are produced inside the narrow confines of the microdischarge filaments and are rapidly lost to recombination outside them.

It is still a matter of scientific debate as to the exact mechanisms which enable a filamentary DBD to be transformed into a homogeneous DBD, but one model proposed (called ‘interpulse preionisation’) is that, for a DBD to be homogeneous, a threshold background concentration of free electrons must be present in the plasma volume at the moment that the driving voltage becomes high enough to trigger ionisation breakdown of the background gas from which the plasma is generated. If such a concentration is present, no preferential current discharge paths present to the applied voltage resulting in spatial constriction but, rather, a discharge current flows across the whole cross-section of the electric field generating a wide area, cool, non-thermal plasma, well matched to the geometry of fabric processing. Certain technological configurations justified by this model, such as the use of helium as a plasma generation gas (with its energetic metastable states supposedly generating free electrons via Penning ionization (see next section 'The atmospheric pressure glow discharge') after the periodic plasma pulse has extinguished, thus creating a free electron reservoir) and restricted driving frequencies, have been shown to result in homogeneous DBDs, but it is unclear whether these in fact constitute justification of the model or are mere artefacts of the particular mode of operation. Artefacts or not, it is these scientific discoveries, such as the importance of helium gas in the generation of well-behaved plasmas, that have had a profound effect on technological development of plasma surface engineering and, daily, point to the direct linkage between fundamental scientific research and industrial manufacturing capability.

An alternative model of homogeneous DBD plasma states that the background electrostatic charge is not important but that the DBD discharge will always be homogeneous if gas breakdown proceeds according to the Paschen Law. As mentioned above, the Paschen Law is founded on a particular microscopic model of gas breakdown called the Townsend breakdown mechanism. This mechanism postulates that gas breakdown under applied voltage occurs because of ionisation of gas neutrals through collision with free electrons energised by the applied electric field. Such collisions, which take place throughout the gas volume to give a diffuse plasma, generate cascades of secondary free electrons which, in turn, become energised and collide, and so on. This homogeneous DBD model indicates that such a breakdown mechanism can be mediated by technological parameters including the electrical characteristics of the dielectrics covering the electrodes and the detailed structure of the driving voltage from the external power supply. The dielectric barriers in this model play a key role in ensuring Townsend breakdown and obtaining a well-behaved, homogeneous DBD. Firstly, they prevent large instantaneous current density in the plasma which, in turn, hinders operation of the competing streamer gas breakdown mechanism. (This is the alternative to Townsend breakdown at atmospheric pressure and relies on propagation of localised avalanches of charge creating narrow current channels between the electrodes, leading to filaments or arcs.) Secondly, charge carriers are stored as trapped surface charge on the dielectric. These trapped electrons are easily mobilised and released into the inter-electrode gap by thermal emission, enhanced by an applied electric field, to act as primary electrons initiating Townsend breakdown to strike a diffuse plasma. Furthermore, the plasma is sustained at lower voltage because of the additional surface charge field which, again, reduces the propensity to streamer formation. Accordingly, the model proposes that the dielectric properties of the bulk insulator covering the electrodes are a decisive parameter for plasma generation and stability.

The above considerations are related to indicate the extent to which plasma technology relevant to textile processing is still exploring both its scientific underpinnings and its industrial development, a situation that offers both challenges and opportunities.

The atmospheric pressure glow discharge

The third APP type intrinsically capable of meeting the size and temperature constraints needed for textile processing is the Atmospheric Pressure Glow Discharge (APGD). This is analogous in its mode of generation and some key characteristics to the famous low-pressure glow discharge plasma that is the backbone of the global plasma industry and workhorse of a dozen major industries, in particular the omnipresent microelectronics industry, which would not exist without the glow discharge plasma.

The APGD is generated by application of relatively low (~200 V) voltages across opposing symmetrical planar or curved electrodes, separated by mm at high frequency, or even very high frequency, radio frequencies 2–60 MHz, much higher than the other plasma types. The electrodes are not covered by dielectric but are bare metal, a feature that enables significantly higher power densities (up to 500 W/cm^3) to be coupled into the discharge than can be achieved with corona or DBD. The APGD is denser than the DBD, with typical free electron densities of 10^{11}–10^{12} electrons/cm^3, but the free electrons are slightly cooler at temperatures of 10 000 to 20 000 K. Textile treatment temperatures can run at 25–50 °C.

APGD plasma takes the form of a bright, uniform, homogeneous glow in the region between the electrodes. The application of voltage between metal plates would generally result in generation of a highly undesirable, very high current density and hot plasma arc. By control of the inter-electrode gap and the frequency of the driving voltage and, above all, by the use of helium as ~99% of the generation gas, arcing is prevented and a large volume, non-thermal plasma is generated, which is both dense and a rich source of the chemical species needed to carry out textile processing. APGD practitioners claim chemical fluxes 100× greater than those available from DBD and 1000× greater than corona. The need to use helium, a finite (given current extraction methods) and increasingly expensive resource, is undoubtedly a commercial issue for APGD in some but not all processes, but this can be addressed by the inclusion of a helium recycling sub-system in the equipment package since helium is not consumed in the process.

It is worth mentioning that the element helium occupies a special place in the science and technology of APP. This amazing gas has several special properties that, in combination, make it uniquely suited for the generation of well-behaved, large volume, cool plasma at atmospheric pressure. Helium has the highest ionisation potential (the energy needed to strip an electron from the neutral atom) of all the elements, which should make it very difficult to breakdown and, hence, to generate helium plasma. However, helium's ionisation cross-section (the probability that collision with another microscopic entity will result in ionisation of the helium atom) is very large because it is a simple atom with very few options for dealing with incoming energy other than ionisation. Other gases, such as oxygen or nitrogen, are microscopically more complex with many different energetic modes, including numerous electronic, vibrational and rotational energy levels so that the cross-section for ionisation of these gases is small relative to the total cross-section for all processes and there is an excellent chance that energy imparted in a collision will be absorbed by a non-ionising process. The large ionisation cross-section of helium results in it being very easy to electrically breakdown at low applied voltage and form plasma, despite the high energy needed to ionise it. Furthermore, helium has long-lived, high energy metastable states that soak up energy from the applied electric field and act as a source of charged species to help maintain the plasma through a mechanism called Penning ionisation. Here, a neutral helium atom in its high energy metastable state collides with another atom or molecule, usually an impurity in the gas such as nitrogen, and gives up its energy by ionising the impurity into an ion and a free electron. Creation of these charged species sustain the plasma and, again, reduce the voltage needed to maintain the discharge, low applied voltage being critical to DBD homogeneity through the avoidance of the 'streamer' mode of gas breakdown in which a surge of charge leaps from one electrode to the other forming high current channels leading to filamentary or even arc discharges. Two further properties of helium are notable, its high thermal conductivity and its chemical inertness. Helium's excellent heat conduction again supports the formation of a homogeneous discharge by quenching instabilities in the plasma due to 'hotspots'. These higher temperature micro-regions can arise in the plasma volume through various mechanisms, such as preferred discharge points on an electrode, and can result in a thermal runaway due to the positive reinforcement of stronger local discharge generating more local heating and so on. The end result is creation of a high current channel filament or arc which the plasma much prefers to discharge through rather than have to spread its current load over a wide area. The helium acts to cool these hotspots by conduction, thus greatly reducing this mode of plasma instability and break-up. Finally, helium's chemical inertness, having essentially no tendency to combine with other elements, is a great advantage to the plasma chemist and process engineer in that it goes some, but only some, way towards decoupling of the physics of plasma generation from the process chemistry giving process designers some additional freedom. All in all, helium has been and continues to be probably the best medium for non-thermal APP research as well as being technologically valuable as a route to useful large volume, cool plasmas.

4.3.3 The glow-to-arc transition

The third physical phenomenon to play a strong role in the exploitation of APP for textile processing is the glow-to-arc transition. This is a notorious instability in atmospheric-pressure plasmas and is the major problem in the generation of large volume, homogeneous, cool APP. The phenomenon is directly related to the current density (A/cm^2) of the plasma. As long as current density remains below a threshold, the plasma remains well behaved, i.e. uniform over a large volume and close to room temperature. However, on passing the threshold for glow-to-arc transition, two changes occur in the plasma. Firstly, the discharge dramatically constricts, shrinking to a fraction of the glow volume. Secondly, the plasma moves from non-thermal equilibrium to become thermal plasma. Both of these effects render the plasma useless for textiles.

This change has many possible origins and a large literature exists on the various instabilities that could lead to the glow-to-arc transition. Early investigations focused on conditions at the electrodes (such as cathode material, uniformity and impurities) that could induce the transition. It later became evident that processes in the plasma could also effect this transition. Analysis of discharge instabilities at the microscopic level is extraordinarily complex, requiring knowledge of the electron production and loss mechanisms in the discharge. However, it is possible to group the instabilities into two types, electronic and thermal instabilities. Thermal instabilities result from changes in the kinetic temperature of the neutral population, whereas electronic instabilities result from changes in the electronic excited state population. In any event, the transition is characterised by increasing rates of collisions between the fast free electrons and the slow cool neutrals. The electrons lose heat while the neutrals and ions gain heat until, in the final arc discharge state, the electron, ion and neutral temperatures in the plasma are equal so that the discharge is at thermal equilibrium and very hot. As part of this process, the plasma density increases by orders of magnitude from perhaps 10^{10} electrons/cm^3 to ~10^{17} electrons/cm^3, thus massively increasing the current carrying capacity of the discharge per unit area so that the plasma can constrict in size while still carrying the same or higher total current load. Free of its obligation to spread out to carry the circuit current because of restricted current density, the plasma collapses into a hot, constricted arc.

Technologically, this means that plasma engineers must design their systems to avoid the glow-to-arc transition and restrain current densities below the transition threshold. This, for example, limits the power than can be coupled into a plasma volume which, in turn, affects plasma chemistry and process times.

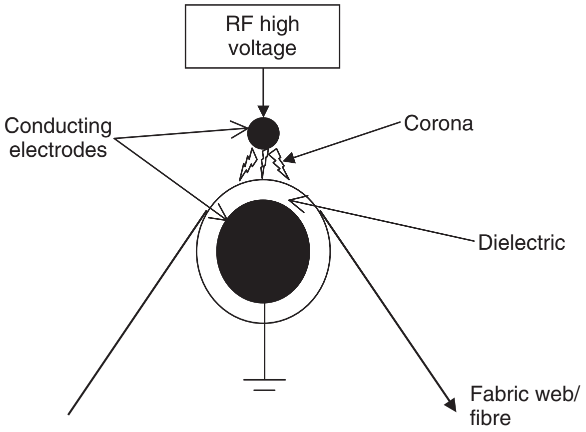
4.3.4 The useful atmospheric-pressure plasma types for textile processing

The constraints imposed on plasma system designers by the physical principles discussed above have resulted in a limited number of plasma types being available for the atmospheric-pressure processing of textiles. These types are described below.

The hybrid corona/DBD

For reasons to do with power sources, ease of plasma generation, robustness, etc., the plasma industry has developed equipment configurations that run a hybrid corona/DBD plasma type that is universally and colloquially called 'corona', with the equipment called a 'corona treater' and the process that it runs called 'corona treatment'. This plasma type will be called 'Corona' from hereon. In fact, the industrial 'Corona' uses elements of both its corona and DBD parents, having the corona plasma type's asymmetric electrode configuration, typically a metal rod opposing a large diameter metal cylinder, together with the DBD's dielectric, generally a ceramic, covering the rod or the opposing cylinder or both. The plasma takes the form of a discharge across the smallest gap, generally about 1.5–6 mm, between rod and cylinder and is short, only some 5 to 10 mm in length in the direction of web travel. Some practitioners would characterise such a short processing length as a major disadvantage of this plasma type but this is not necessarily the case, the required fabric residence time in the plasma depending completely on the target process and the capability of the equipment to deliver power into the fabric. The web to be processed runs over the cylinder and through the plasma region with the plasma typically taking the form of bright, discrete microdischarges crossing the gap normal to the electrodes. If the gas from which the plasma is generated is ambient air, the microdischarge filaments can be close together but distinguishable. If other gases are used, the filaments can close up until the plasma takes the appearance of a continuum. The Corona Treater is typically driven by an a.c. power source generating applied voltages across the electrodes from ~1–10 kV peak-to-peak at 10–50 kHz frequency (see Fig. 4.2).

This hybrid plasma type has been technologically exploited to deliver highly robust equipment configurations that have been in mainstream production in several industries, not including textiles, since the 1950s and, indeed, was the only non-thermal APP type in industrial production for



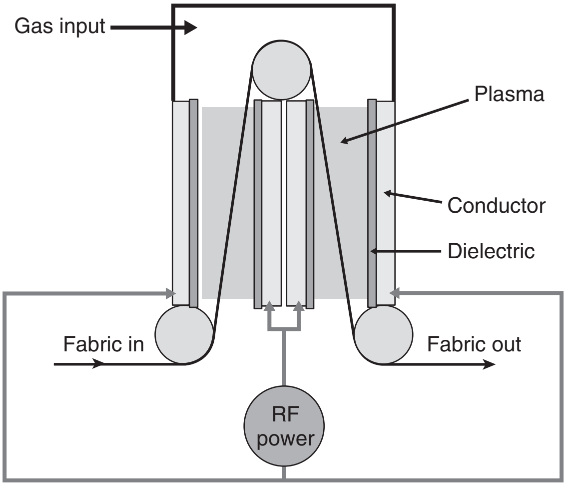
4.2 Cross-section schematic of a covered roll Corona system.

around half a century until the new millennium. A range of plasma providers offer equipment configurations based on 'Corona' that now have relevance to textile processing. These include (as at 2006) Enercon of the US, Ahlbrandt of Germany, Vetaphone of Denmark and Softal of Germany, and they are discussed in the following section.

The homogeneous DBD

Relative to the hybrid corona/DBD plasma type, the two remaining APP types are newcomers to the APP industrial processing scene. The first of these is the homogeneous DBD. A single plasma systems provider, Dow Corning Plasma Solutions[2] of County Cork, Ireland, currently (2006) offers this for textile processing with technology originally developed by Plasma Ireland Ltd. The homogeneous DBD plasma is readily generated between symmetric, large area (m^2), opposing parallel plate electrodes in compliance with technological criteria. These include careful selection of generation gas, typically helium, argon or, possibly, nitrogen or mixtures of these, minimisation of generation gas impurities through largely eliminating influx of ambient air into the plasma region, incorporation of the right dielectrics in terms of electrical and mechanical properties into the large area electrode systems and use of matched frequency and power configurations in the application of driving power. The results are truly large area (e.g. 2 metres wide, 10+ metres long in the direction of fabric travel), ~6 mm thick, cool plasmas well suited in manufacturability terms to the processing of textile webs.

Figure 4.3 shows a cross-section schematic of Dow Corning Plasma Solutions' homogeneous DBD generation configuration.



4.3 Cross-section schematic of Dow Corning Plasma Solutions' homogeneous DBD generation configuration.

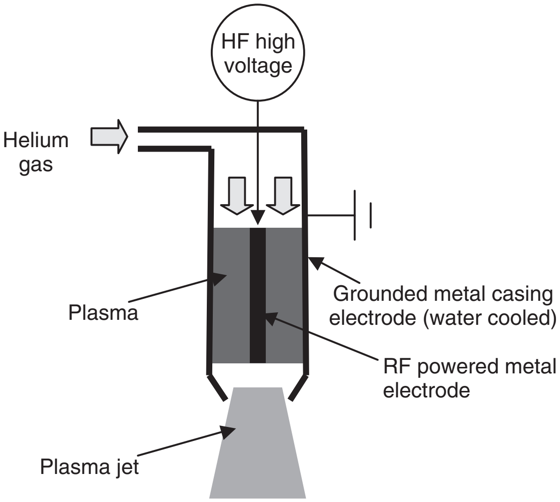
The atmospheric-pressure glow discharge

The second relative newcomer to the APP industrial processing scene is the atmospheric-pressure glow discharge (APGD). Again, currently, a single plasma systems provider, APJeT[11] of New Mexico, USA uses the APGD plasma type for textile processing. This is done using a particular source configuration technology and method of plasma generation called APPJ®. APJeT's APPJ® technology enables plasma to be applied to textile fabrics in the *in-situ* mode in which the fabric is passed through the plasma generation region between electrodes. Figure 4.4 shows a cross-section schematic of an APPJ® system suitable for wide area processing.

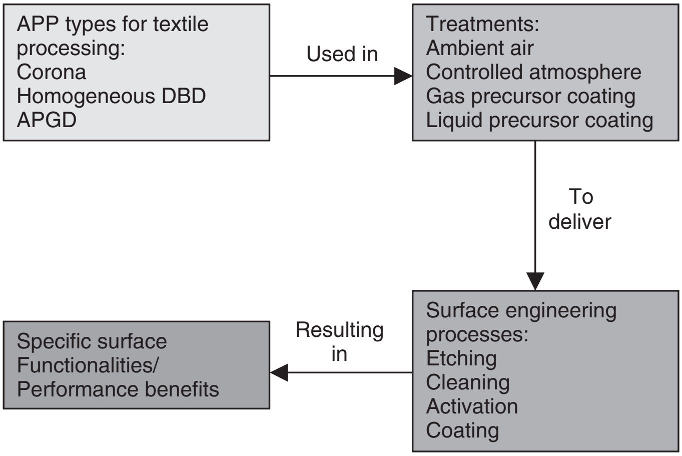
Equipment configurations implementing these plasma types in industrial manufacturing systems will now be reviewed but, firstly, let us understand the linkages from plasma types through to the final product being purchased by the textile manufacturer, namely the specific surface functionality required to meet his/her needs. Figure 4.5 is a schematic showing the flow from plasma type to surface product.

In the following sections, we will look at equipment configurations implementing the relevant plasma types and how they run treatments to deliver surface engineering processes resulting in the specific surface functionalities that, ultimately, the textile manufacturer is buying.

Let us also understand what it is that that the textile manufacturer implementing a plasma-based process in the manufacturing, as opposed to R&D or pilot production, context should be buying from the plasma solutions provider:



4.4 Cross-section schematic of an Atmospheric Pressure Glow Discharge plasma generator.



4.5 The chain APP types to surface function.

- processing equipment, plus
- guaranteed turnkey process delivering the target surface functionality
- at the target cost
- and meeting the target manufacturability requirements.

Each component of the solutions package is critical.

4.4 Atmospheric-pressure plasma equipment for textile processing

The APP equipment configurations for textile processing can be categorised according to the generic treatments that they can run and hence the kinds of surfaces that they can deliver. There are four main treatments:

- ambient air treatment
- controlled atmosphere treatment
- gas precursor coating
- liquid precursor coating.

These are listed in broadly ascending order of process sophistication but it is crucial for the textile manufacturer to understand that process sophistication does not of itself determine the optimum solution meeting his/her specific need. The term 'process sophistication' really means degree of treated surface functionality or performance, as surface functionality/performance is ultimately what the textile manufacturer is buying from the plasma provider. It is therefore critical, if the textile manufacturer is to maximise the cost effectiveness of the purchase, that he/she clearly defines the surface property required in all its aspects, technical and commercial, and then locates the plasma product (equipment plus turnkey process delivering guaranteed surface property at the agreed cost and manufacturability levels) that meets that need exactly, no more and no less. A less sophisticated process will fail to meet the performance criteria required from the treated surface, while a more sophisticated process will constitute over-engineering and incur a cost penalty. In essence, do not buy a gas precursor coating system if an ambient air treatment will meet your need.

Table 4.2 matches the four generic treatments with the three useful APP types for textile processing. It is important to state that this table is not

Table 4.2 Four generic treatments matched against the three useful APP types for textile processing

APP types	Treatments
Corona	Ambient air treatment Controlled atmosphere treatment Gas precursor coating Liquid precursor coating
Homogeneous DBD	Controlled atmosphere treatment Gas precursor coating Liquid precursor coating
APGD	Controlled atmosphere treatment Gas precursor coating

saying that the plasma types are equivalent in their ability to deliver surface functionality. For example, the homogeneous DBD can deliver more sophisticated coatings than Corona, although both can use liquid precursors in different ways. This will become clearer as we proceed through the analysis to describe the specific surface functionalities delivered by the different plasmas.

Corona systems

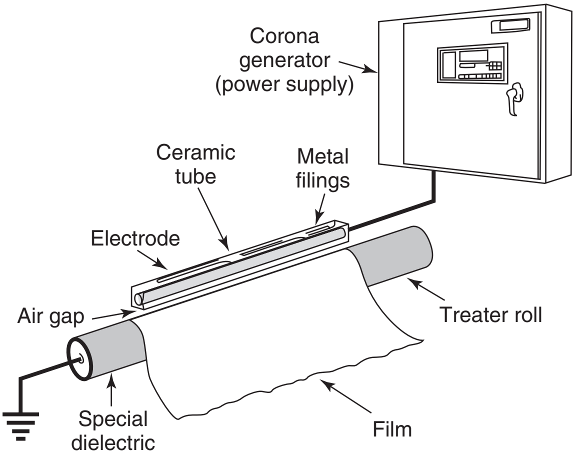
A corona treating system consists of two major components, the power source, and the treater station:

- The power source, commonly referred to as the power supply or generator, generally comprises a high frequency generator and a high voltage output transformer. The purpose of the power source is to raise the incoming electricity (typically 50/60 Hz, 230/460 V) to a higher frequency (10–35 kHz) and higher voltage (10 kV). Typically, power supplies are rated in kilowatts (kW) and can range from 500 W to 30 kW, depending on the application. The generator supplies this power to the treater station.
- The treater station, in turn, applies this power to the surface of the material, through an air or other gas gap, via a pair of opposing electrodes, one at high potential and the other, usually a roller which supports the material, at ground potential. The high electric field between the electrodes breaks down the air/gas thus generating the plasma discharge. A solid dielectric material is needed to cover at least one of the two electrodes in order to generate a corona discharge throughout the inter-electrode gap rather than a narrow, hot arc. Figure 4.6 is a schematic of an industrial Corona treater and Fig. 4.7 shows an Enercon universal treater installed at a customer facility.

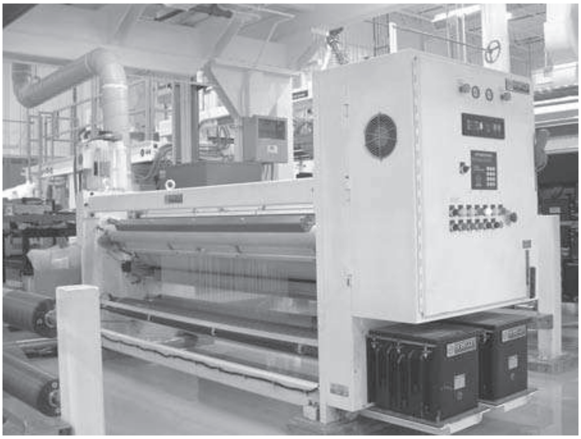
Generally, treater stations come in two configurations, ‘covered roll’ or ‘bare roll’. Covered roll stations have the dielectric covering on the ground roll and the high voltage electrode is bare metal. In contrast, bare roll stations have the dielectric covering on the high voltage electrode and the ground electrode is bare metal. Each type has advantages and disadvantages, as listed in Table 4.3.

Figure 4.8 shows an Enercon bare roll surface treater in action. In the textile context, conducting materials will be very uncommon so that the covered roll configuration is likely to be the preferred option.

Since the energy coupled into the fabric per unit area (J/m^2) is a critical process control parameter in all plasma surface engineering, a corona treater system must be ‘sized’ to the particular application. In the case of corona being used to run surface activation processes, for example, it is



4.6 Schematic of an industrial Corona treater (Courtesy of Enercon Industries Corporation[3]).

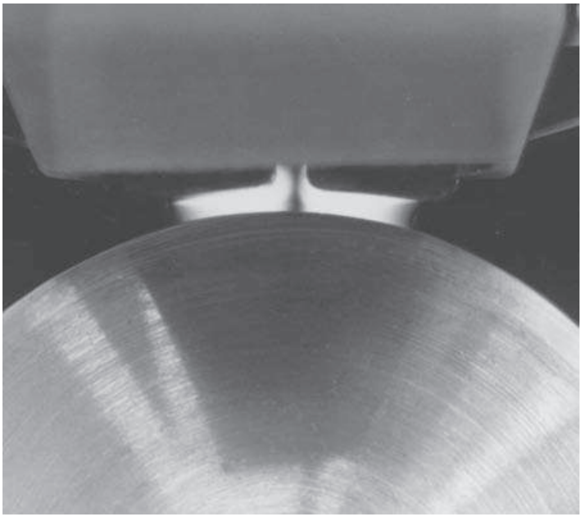


4.7 An Enercon universal treater installed at a customer facility (Courtesy of Enercon Industries Corporation[3]).

necessary to first determine the target surface energy or surface tension needed. The measure of surface energy used is called the 'dyne level' with units of mN/m (milli-Newtons per metre) or dynes/cm; these are equivalent and correspond to energy/unit area (J/m^2). Next, the 'watt density' that will be needed to raise the dyne to the desired level for a particular material is found from empirical tables and this is multiplied by the width of the material and the line speed to determine the maximum total power in kW needed for the application. This kW level determines the size of the power

Table 4.3 Advantages and disadvantages of covered roll as against bare roll treater stations

	Covered roll	Bare roll
Advantages	• More efficient than bare roll • Will work on difficult materials • Designed for non-conductive materials • Easy to adjust treat width and to lane treat specific areas leaving other areas untreated • Can vary dielectric coverings to meet cost, durability, size and treatment • Can treat any width material	• Can treat conducting materials • Smaller than covered roll stations • Easy repair of dielectric failure on electrodes
Disadvantages	• Cannot treat conducting materials • Dielectric failure requires tedious roll removal • Larger than bare roll stations	• Less efficient than covered roll • Will not work on difficult materials • Not easy to adjust treat width or lane treat • Limited to about 3 m treatment width • Requires large volumes of air/gas for electrode cooling



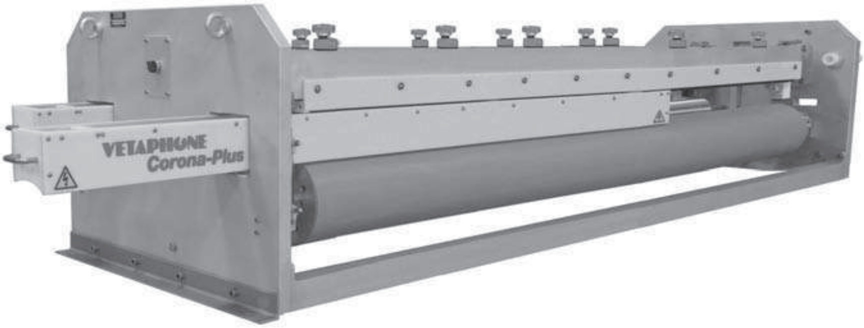
4.8 Enercon's Bare Roll Surface Treater in Action. (Courtesy of Enercon Industries Corporation[3].)

supply, the electrodes and treater rolls and, thus, the overall specification of the corona system.

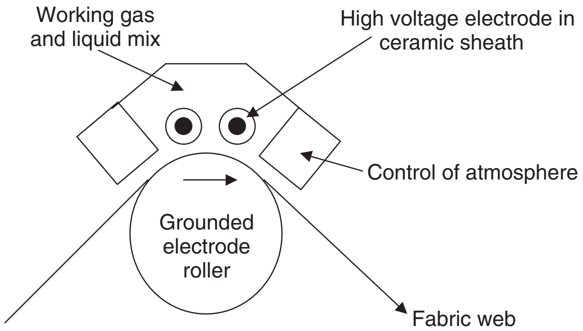
A by-product of corona treatment where air or oxygen is the plasma generation gas is the generation of ozone (O_3). This must be removed from the work area as it is a health hazard and causes serious corrosion problems. Increasingly stringent air pollution regulations are preventing exhausting into the atmosphere and it is now generally necessary not merely to extract ozone from the work area but to destroy it. This is achieved by converting ozone into oxygen using a metal oxide bed catalytic ozone decomposer which is an essential item of ancillary equipment for the corona purchaser.

A wide range of companies supply corona treatment systems ranging in width from a few hundred mm to over 10 m and running at speeds from tens of metres/minute to >1000 m/minute depending on the material and process, many with special features tailored to the material and application. Corona is a mature, robust and industrially proven manufacturing technology that has been widely used for decades in the treatment of all kinds of films, foils and webs but by no means all systems are suitable for textile processing. In fact, corona systems suitable for textile treatment tend to be specialised and not offered by all corona system providers. Some current corona equipment suppliers who claim textile processing capability include:

- Enercon Industries Corporation,[3] Menomonee Falls, WI, USA
- Vetaphone A/S,[4] Kolding, Denmark (Figure 4.9)
- Ahlbrandt System GmbH,[5] Lauterbach/Hessen, Germany
- Softal Electronic,[6] Hamburg, Germany
- Pillar Technologies,[7] Hartland, WI, USA
- AFS Entwicklungs- und Vertriebs GmbH,[8] Neusaess, Germany
- Sigma Technologies International, Inc.,[9] Tucson, AZ, USA.



4.9 The Vetaphone TOW8 Corona-Plus System showing power supply and treater station. (Courtesy of Vetaphone A/S[4].)

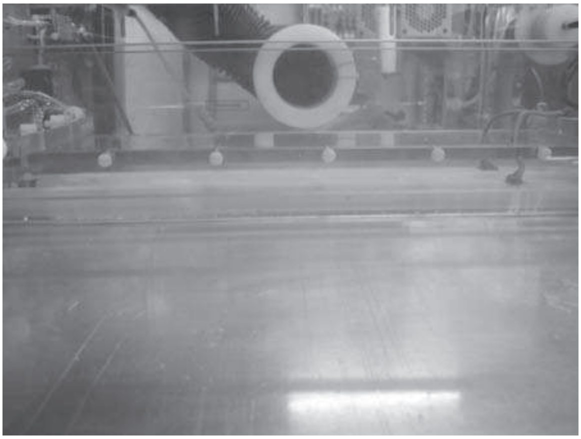


4.10 Cross-section schematic of a Controlled Atmosphere Corona system.

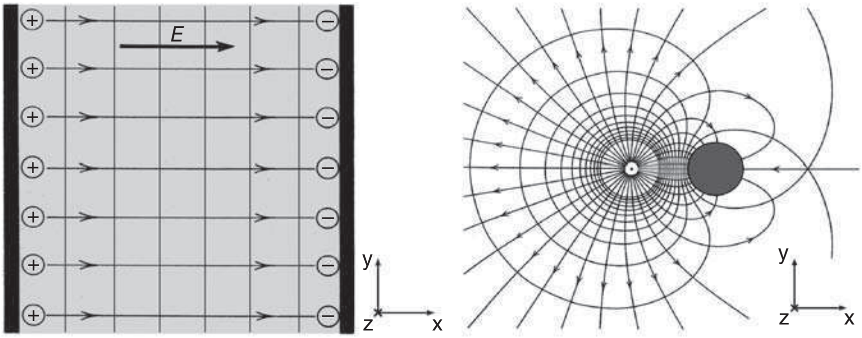
The very large, even overwhelming, majority of corona systems sold into multiple industries run on ambient air to deliver a surface activation process resulting in increased surface energy. However, an important and growing class of corona systems for activation of difficult materials and for new processes offered by several of the above companies employs some form of containment around the plasma region combined with a gas delivery system. These are especially relevant for textile treatment. The aim is to create an air-free atmosphere in a limited zone while still allowing free passage of the fabric through the plasma. The containment typically comprises a hood surrounding the electrodes together with the backing roller grounded electrode leaving open slits for the web to pass. By filling the containment region with selected gases, a well-defined, controlled gas atmosphere is produced from which different atmospheric pressure plasma chemistries are generated. This allows control over the plasma chemistry and, hence, surface reactions, thus enabling corona to carry out the controlled atmosphere treatment and the gas precursor coating generic treatments. Figure 4.10 is a cross-sectional schematic showing the concept. Not only can the gas atmosphere be controlled, but liquid precursors can be introduced into the working region in the form of a mist of atomised droplets to participate in the plasma chemistry. A slightly different geometry using the same concept is to replace the roller with a metal plane. The Danish company Vetaphone[4] employs this as well as the roller systems (see Figure 4.11).

Homogeneous DBD systems

The geometry of the homogeneous DBD equipment currently on the textile processing market is very different to that of Corona. It is characterised by symmetrical planar electrodes opposing each other across a gap of ~10 mm.



4.11 Side view of two enclosed powered electrodes opposing a flat plane generating Corona in a controlled atmosphere of nitrogen. (Courtesy of Vetaphone A/S[4].)

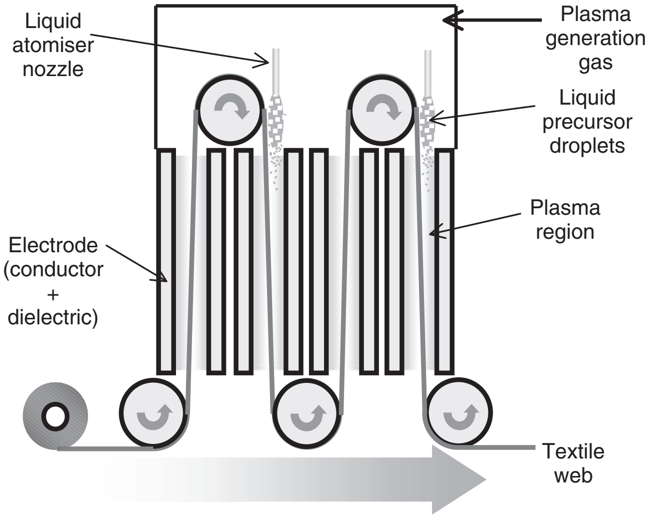


4.12 Plasma regions in grey – homogeneous DBD (left) vs. conventional corona (right). (Courtesy of Dow Corning Plasma Solutions[2].)

These electrodes are of truly large area, metres in width but also metres in length along the direction of travel of the fabric. Figure 4.12, a cross-section schematic through the electrodes, shows the differences in geometry and size of the plasma regions between homogeneous DBD and corona. The lines are electric field and equipotential.

Typically, both electrodes are covered by dielectric and a low frequency RF (~50 kHz) voltage of around 10 kV applied across the electrodes strikes the plasma, filling the entire inter-electrode region with a uniform, homogeneous glow. This region is filled with a selected plasma generation gas, often called the 'ballast gas', such as helium, argon, nitrogen or mixes, chosen for its propensity to generate well-behaved, large volume, cool APP and to facilitate control of the plasma and, hence, the process chemistry. In addition to the ballast gas, which is generally chemically inert or of low reactivity, special gas or vapour additives such as oxygen or CF_4 can be added to the gas stream in order to carry out a particular chemistry and deliver a specific surface effect.

The electrodes are set up vertically to avoid sag distortion arising from their own weight, to minimise footprint and to aid confinement of gas using the principle of relative density in which helium, for example, will tend to stay confined in a box geometry open only at the base. Figure 4.13 is a schematic cross-section showing the textile web processing configuration used by the manufacturer of this technology, Dow Corning Plasma Solutions.[2] This particular system consists of four vertical plasma regions or 'legs' each sandwiched between a pair of vertical electrodes and through which the fabric or yarn is guided by rollers, entering and exiting the system at the open base in a manner fully compatible with continuous, on-line production. The plasma generation gas is introduced from the top, and what is particularly significant in this version of the kit is the introduction of liquid precursor by way of atomised droplets into two of the legs. Thus, the process chemistry can be controlled through gas and vapour precursors or



4.13 Cross-section schematic of a 4-plasma region large area homogeneous DBD generator. (Courtesy of Dow Corning Plasma Solutions[2].)

through liquid precursors or a combination. This flexibility gives this system probably the widest range of functionalisation capability of any of the APP equipment options. Functionalisation can range from simple oxygen-based surface activation through controlled atmosphere treatment to gas precursor functional coating and liquid precursor coating.

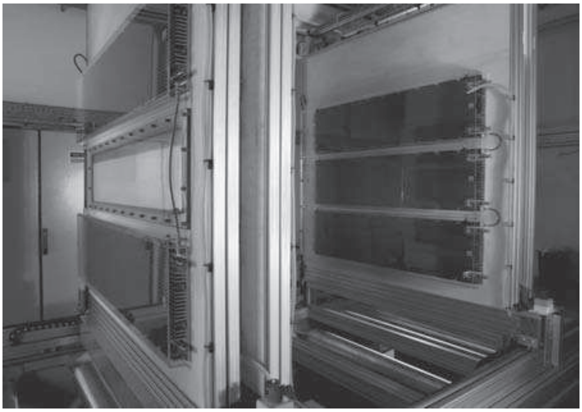
It would not make commercial sense to use such a system for oxygen-based activation alone when a standard air Corona system would do the job at much lower cost and faster line speed, but it would make sense to run such an activation step in this homogeneous DBD system as part of a multi-step process. This is one of the advantages of the homogeneous DBD configuration, namely that it allows multiple plasma regions to be stacked in series, each one of which has a large degree of process independence from the others. Thus, for example, the first leg of the above system could be used as a purge to remove trapped and entrained air from the fabric, the second leg could run an activation process, while the third and fourth legs could put down two different functional coatings in succession by firing into the respective regions different liquid precursors such as an adhesive primer followed by an oleophobic coating for durable anti-dirt and stain proofing.

A particular advantage of this equipment configuration is the long plasma path length in the direction of travel of the fabric. This can extend to metres or even tens of metres. Thus, for a given line speed, the residence time of the fabric in the plasma can be extended, enabling more energy per unit area to be coupled into the material and/or a thicker coating to build up. Alternatively, for a given residence time, the line speed can be increased by increasing path length.

The interfacing of metal electrodes to dielectric, essential to the homogeneous DBD system, has proven to be somewhat problematical. The bonding is tedious and the different coefficients of thermal expansion of metal and insulator can lead to delamination and separation over time. Dow Corning Plasma Solutions has developed an ingenious and successful improvement by replacing metal with salt water. Brine is sufficiently conductive to act as an electrode, requires no bonding, remains in permanent intimate contact with the ceramic dielectric and contains no edges, corners or other singularities which can act as high-voltage discharge points, generating unwanted electrical discharge outside the plasma region. Furthermore, the salt water acts as a heat sink, removing from the dielectric in contact with the plasma the slight heat generated by the plasma. This is done through simple air cooling fins in contact with the brine so that there is no long term heat build-up in the system. No water cooling is needed and the air cooling flow required is modest. This is in contrast with some corona systems that require high air-cooling flow and APGD systems that need water cooling.

Figure 4.14 shows the Dow Corning Plasma Solutions[2] SE-1000 AP4 flexible web processing system. Figure 4.15 is the realisation of the schematic shown in Figure 4.13 and shows a close-up of four plasma region 'legs', i.e. four pairs of opposing vertical electrodes each pair with a small gap between them. The 'legs' themselves are also grouped in pairs, with the first pair (running alongside the central vertical axis of the photograph) separated from the second pair (on the extreme right of the photograph). Plasma is running in the first leg as seen through the central window.

4.14 The Dow Corning Plasma Solutions SE-1000 AP4 large area web processing system showing front view of vertical electrode and control cabinets. (Courtesy of Dow Corning Plasma Solutions[2].)



4.15 The Dow Corning Plasma Solutions SE-1000 AP4 system showing an angled view of the four vertical electrode sets with the homogeneous DBD plasma seen through the window of the first leg. (Courtesy of Dow Corning Plasma Solutions[2].)

Atmospheric-pressure glow discharge systems

A single supplier, APJeT[11] of New Mexico, USA, offers their APPJ® technology for textile processing using this plasma type. The plasma generation scheme is implemented in the form of a flat jet which can be built up to about 5.5 m in width and allows the fabric to be passed between the electrodes, through the plasma generation region, to be treated *in situ*. Units can be flexibly ganged together to make up a complete textile processing system. The TexJet unit is APJeT's flagship production-scale product, designed to treat textiles and non-wovens at speeds of up to 120 ft/minute. It has a small footprint of 8-ft high by 8-ft wide by 3-ft deep and is typically equipped with eight 6-ft wide flat jet electrodes. Fabric enters the TexJet machine through a pre-treatment processor, which removes excess moisture and entrapped air without the use of vacuum. The fabric is then plasma-treated *in situ* by each of the eight 10 kW units. Designs can be varied from 20 to 120 kW. Fabric may be treated on one or both sides.

The particular mode of generation of the plasma type requires that helium be >95% of the plasma generation gas. Because of the cost of helium, this can motivate inclusion of a helium recycling unit into the capital equipment specifications, readily supplied by APJeT's strategic partner, Air Products & Chemicals, Inc.,[10] and which should be factored into the cost equation.

4.5 Atmospheric-pressure plasma surface properties for textile products

After all the description of the underlying physics and equipment engineering of APP, what is important to the textile manufacturer is what he/she is ultimately buying. This is, of course, surface functionality, and the power and attraction of APP is its ability to deliver a huge variety of chemically and/or physically active and valuable functional groups incorporated into and onto the textile surface to deliver specific properties. Many of these are described elsewhere in this book so the following overview is in no way comprehensive or exhaustive.

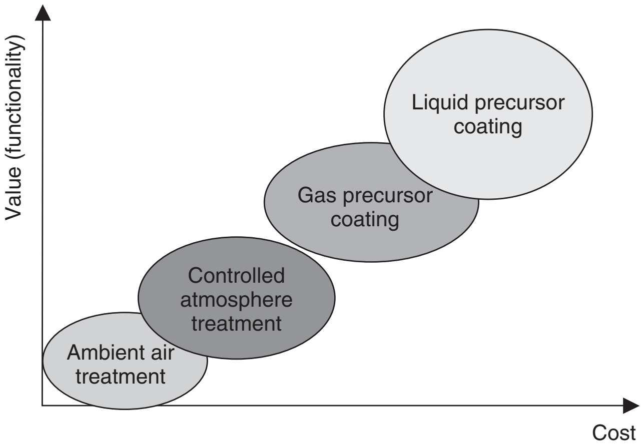
To recall, plasmas are used to deliver these surface properties because they provide a rich source of chemically active species that react with a surface or react with each other to produce secondary, short-lived chemical precursors needed for thin film deposition. The success of APP processing technology stems from its low temperature, continuous, on-line operation combined with the fact that no other method can provide the same nondestructive materials treatment capability.

A key distinction between the different APP options is how they perform in relation to the critical ratio – added value/cost. Added value is strongly related to surface functionality or performance; the more sophisticated and powerful the properties of the treated surface, generally the higher its value to the product. Thus, the chart in Fig. 4.16 is a very rough positioning of the generic treatments available from APP in the functionality (value) vs. cost parameter space.

It is important not to extend this principle beyond satisfaction of the targeted need. There is no added value to be gained and probably a cost penalty by over-engineering a surface. Nevertheless, in general, the degree of functionality or performance achievable from a particular plasma process product relative to the unit cost of production will distinguish it from its competitors.

The generic surface engineering processes available to the textile industry from the APP treatments can be categorised as etching, cleaning, activation or coating. These processes directly result from the immersion of the textile surface into the plasma and the resulting bombardment of the surface with fluxes of microscopic species carrying physical and chemical energy, particularly chemically reactive species with energies high enough to dissociate and form chemical bonds. Such species, which are generated by the ionisation, fragmentation, and excitation processes resulting mainly from collisions with high-energy free electrons accelerated by the applied electric field, include fast free electrons, ions, UV photons, radicals, excited states (electronic, vibrational and rotational), molecular fragments, etc.

- *Etching*, the removal of bulk substrate material, occurs when the interaction between the solid surface and the plasma generates gas-state by-products, which include atoms or molecules, from the substrate. These desorb from the surface and are carried away from the substrate, thus removing bulk material.



4.16 An approximate positioning of the generic APP textile treatments in the Value vs. Cost parameter space.

- *Cleaning*, the removal of contamination, is a form of etching but with very high selectivity. Essentially, only the unwanted surface contaminant is volatilised and removed while the substrate remains untouched by the process.
- *Activation*, enhancement of the surface energy, is the generation of chemically reactive sites on a previously unreactive surface resulting in a rise in surface tension.
- *Coating*, deposition of a functional thin film, occurs if the plasma–solid surface interaction creates a solid phase material. This remains on the surface and agglomerates over time, e.g. micro-seconds, to generate a conformal film. This process is sometimes called Plasma Enhanced Chemical Vapour Deposition (PECVD) or plasma polymerisation.

It is important to emphasise again that these APP processes are confined to a very few atomic monolayers of the substrate surface, ensuring that the bulk of the substrate remains totally unaffected, thus allowing a decoupling of the surface properties from the bulk properties of the material and giving the textile product designer a major new degree of freedom.

We have seen in the previous section how the three useful APP types for textile processing are used in generic treatments. Table 4.4 lists the surface engineering processes delivered by each of the treatments. Again, this table emphatically does not state that the treatments are equivalent. It simply says that each treatment can, to certain materials and given the right

Table 4.4 The surface engineering processes that can be delivered by each of the three APP types useful for textile processing

APP types	Treatments	Surface engineering processes
Corona	Ambient air treatment	Cleaning Activation
	Controlled atmosphere treatment	Etching Cleaning Activation
	Gas precursor coating	Coating
	Liquid precursor coating	Coating
Homogeneous DBD	Controlled atmosphere treatment	Etching Cleaning Activation
	Gas precursor coating	Coating
	Liquid precursor coating	Coating
APGD	Controlled atmosphere treatment	Etching Cleaning Activation
	Gas precursor coating	Coating

conditions, carry out the generic process to some degree. The power and sophistication of the treatments for each APP type is, in general, listed in ascending order in the table. Thus, for example, the cleaning and activation process capabilities of controlled-atmosphere treatment are significantly superior to those of ambient air treatment and the coatings available from liquid precursors can be of higher molecular weight and greater sophistication than those from gas precursors. But, again, it all comes down to matching the solution to the need.

All textile materials, natural or synthetic, are amenable to these APP treatments including polypropylene, polyethylene, polyester, polyaramids, nylon, wool, linen and cotton.

We will now outline the specific capabilities of each of the treatments in terms of their surface engineering processes and the specific surface functionalities/performance benefits that they can deliver.

4.5.1 Ambient air treatment

Ambient air treatment, where APP is generated from the factory air environment, is the only process to be run by a single APP type, namely corona. Line speeds depend on the material and degree of activation required and vary from 50 to >500 m/minute. The process essentially enhances surface energy. The plasma can achieve this by both cleaning the surface and by activating it. The essence of a successful APP treatment targeting wettability and adhesion is to remove loosely bonded surface contamination and to introduce stable chemical functionalities providing nucleation and chemical bonding sites for subsequent over-layer deposition. As is discussed below, the abilities of the various APP treatments to achieve this can be ranked in ascending order of effectiveness as ambient air treatment < controlled atmosphere treatment < gas precursor coating < liquid precursor coating. The correct choice of treatment depends on the textile material and the target coated system performance parameters.

A limited number of organic surface contaminants can be reduced or removed by air corona treatment and surface activation takes place, as shown by simple surface energy tests such as the contact angle of water and solvents. Several models are advanced to account for this phenomenon, including micro-roughening enabling enhanced physical ‘keying’ into the surface and the electret effect where polymer chains of the substrate are carbonised to create reactive sites. But the most commonly accepted model appears to be that of high-speed oxidation. The model states that the corona energy breaks molecular bonds on the surface of non-polar substrates, which broken bonds then recombine with free radicals in the corona environment to form polar groups on the film surface. These polar groups have strong chemical affinity to polar coatings, inks, adhesives, etc., resulting in improved adhesion. Similarly, the polar surface results in an increased surface energy, correlating with improved wettability.

The consequences of enhanced surface energy are multiple and of great interest to textile manufacturing. These are improved wettability and, particularly, adhesion. These, in turn, go to important product features and benefits in operations such as printing, dyeing, gluing, coating and lamination. Unlike the purely mechanical bond, as in the case of an ink penetrating into a porous surface such as cotton, APP surface activation delivers a chemical bonding between substrate and coating, ink, adhesive, etc.

Additional surface functionalities and benefits from ambient air treatment are biocompatibility and sterilisation. The removal of surface contaminants and the enhancement of surface energy will generally render low energy materials more amenable to bio-species, although the severely limited chemistry available from air activation greatly restricts this facility, a problem progressively lessened by the rapidly increasing functional capability of the other APP treatments in Table 4.4. With regard to sterilisation, all atmospheric pressure plasmas produce active species that are sterilising agents, e.g. UV radiation, atomic oxygen, ozone, high energy ions and free electrons. All these can rupture molecular bonds and denature proteins, thus offering powerful and environmentally friendly fabric sterilisation processes.

However, it should be said that ambient air treatment produces the weakest effect of the APP treatments, particularly in terms of adhesion and wettability. The effect can be sufficient for a limited number of materials in limited applications but for many, if not most, materials and applications it fails to deliver the performance needed. Adhesion is generally the key need of the corona treatment user and it is important to state that adhesion is a function of both wettability and bond strength between substrate and coating, adhesive, lamination, etc. While ambient air corona treatment will produce improvement in wettability, its effect on bond strength can be negligible. Indeed, ambient air corona can generate a weak boundary layer on the treated surface resulting from low molecular weight fragments. Material adhered to this weak boundary layer produces low adhesion. But, again, this does not mean that ambient air corona cannot meet the textile manufacturer's needs. If the materials and application are right, it will provide a highly cost-effective solution. It is a question of undertaking detailed trials of all possible options to locate that delivering the required technical performance at the lowest cost.

Time and post-plasma handling of the APP ambient air plasma-treated material degrades the effect. The time constant of reduction in properties varies according to the material and its storage and is driven by diffusion of the high energy surface radicals, the re-orientation and folding under of the surface layers and the availability of reactive species from the atmosphere. In humid, exposed-to-sunlight conditions, a corona treated surface can lose >50% of its dyne level surface tension in 10 days or less. More serious is the effect of rewinding the treated fabric onto itself after plasma treatment. Essentially, the APP has produced an active surface looking to bond. If the first contact offered is the rewound material, there will be a major loss of reactive sites as the activated surface bonds to the same material offered in the rewound reel. This strongly motivates users of ambient air corona to place the process in-line so that the first reagent offered to the active surface is the targeted coating, ink, adhesive, glue, etc. Once the final converting process has been performed (printing, coating, laminating, etc.), the bonding becomes permanent, i.e. the ink will not peel, nor will two substrates delaminate. Degradation of ambient air treatment occurs only between the time of APP activation and the following converting process so that delay between time of APP treatment and time of use is a major issue for the textile manufacturer.

It is important to point out that this issue of treatment lifetime is not the same for all APP treatments. The lifetime of controlled atmosphere activated products is typically far longer than ambient air activated surfaces and the functional coatings delivered by gas and liquid precursor coating treatments are permanent.

A further disadvantage of ambient air corona is the possibility of pinholing. Reference has been made to the energetic microdischarges which form this APP type. These can be too energetic and hot for lightweight, sensitive materials resulting in the burning of pinholes in the substrate fabric. This is by no means universal and is highly material and process specific. But, the issue should be investigated by empirical trials if APP ambient air treatment appears to offer the textile manufacturer the most cost effective solution meeting target needs.

In summary, APP ambient air corona treatment may meet some textile processing needs but is highly limited in its capabilities and will probably not feature significantly in mainstream textile manufacturing.

4.5.2 Controlled atmosphere treatment

In moving from ambient air to controlled atmosphere, the APP practitioner is vastly enhancing his/her process capability. Stating the obvious, the controlled atmosphere treatment system has freedoms not available to ambient air systems, namely the ability to customise the plasma, and hence process chemistry, to get the best result from the particular substrate. Typical key treatment control parameters are input power, gas types and ratio of gas mix, gas flow and fabric line speed. The principal processes available from this APP treatment are, again, cleaning and activation aimed primarily at adhesion. But there is also interest in the generic process of etching.

Almost all of the plasma system manufacturers mentioned previously offer controlled atmosphere treatment from their systems, in which the ambient air in the plasma generation region is replaced by selected gases. Thus, for example, certain corona systems of Enercon[3] and Vetaphone,[4] the homogeneous DBD systems of Dow Corning Plasma Solutions[2] and the APPJ® technology of APJeT[11] all run controlled atmosphere treatment at line speeds which are system and process dependent but are in the range 30–350 m/minute. Typically, the atmosphere comprises a ballast gas forming the large majority (>90%) of the total gas flow. The ballast gas is generally selected for its chemical inertness and its propensity for generating well-behaved APP; helium, argon and nitrogen are the usual candidates. Generally, but not always, small amounts, typically 1–10%, of chemically reactive gas (includes vapour) or gas mixes, are added to the gas stream. Examples are oxygen, nitrogen, carbon dioxide, ammonia, hydrogen, water, fluorine and tetrafluoromethane.

The process proceeds through plasma bombardment of the surface creating reactive bonding sites, the generation within the plasma itself of active species and the grafting of functional groups to the surface. The process can also produce bond scission and cross-linking of the treated surface. The resulting surface functionalisation depends, of course, on the gases used. A survey of the literature reveals a wide range of surface functionalisations achieved by APP controlled atmosphere treatment. A few examples to give the flavour are:

- Helium/oxygen plasma treatment of PP introduces oxidised functional groups onto the surface, which may include alcohol, ketone, carboxy, ether, ester or hydroperoxide.[3] The introduction of polar groups onto the PP fibres allows chemical bonding with, for example, dye molecules, in contrast to the untreated PP molecular chains which are non-polar giving a hydrophobic surface.
- Oxygen and oxygen-containing plasmas impart functional groups such as $C—O$, $C=O$, $O—C=O$ and $C—O—O$, as well as surface etching of fibres, all enhancing wettability and adhesion characteristics.
- Fluorine and fluorine containing gases (CF_4, C_2F_6) result in the incorporation of fluorine into the surface, resulting in hydrophobicity.
- Nitrogen and ammonia plasmas introduce amino ($—NH_2$) and other nitrogen containing functionalities onto natural and synthetic fibres. On wool, these are dye sites increasing dye absorbtion.
- Treatment of PTFE with hydrogen-containing plasmas such as forming gas (N_2/H_2::95%/5%) and ammonia results in large increase in surface energy due to a high defluorination rate resulting in the formation of $C—C$, $C—H$ and $C=C$ bonds and cross-links, and to nitrogen and oxygen species grafted onto the treated surface.

Electron microscopy of controlled atmosphere-treated fibres shows a uniform and homogeneous cleansing of contaminants and a micro-roughening of the surface. Both of these effects enhance wettability and adhesion.

In addition to cleaning and activation, controlled atmosphere APP can etch the substrate fibres either through a physical effect in which high energy ions 'sputter' material out of the surface, i.e. knock out molecules through transfer of kinetic energy and momentum, or through chemical reaction resulting in the formation of volatile compounds containing substrate species which desorb from the surface and are carried away by gas flow. Resulting surface effects include micro-roughening, shrink proofing and size removal.

Micro-roughening tends to enhance adhesion and, particularly when combined with deposition of a hydrophobic coating, can produce through the 'lotus effect', a self-cleaning property where dirt particles are easily removed from the surface by water droplets.

Shrink proofing of wool is achieved by APP oxygen and nitrogen based plasmas. These etch the fibre surface and also generate reactive sites where sliding fibres tend to stick, both of which increase the overall coefficient of friction thus reducing the directional friction effect, the cause of wool felting. The process also etches and softens the fibre scales that produce the directional frictional effect. When combined with post-APP application of a thin resinous coating which smooths out the fibres, the combination treatment produces a shrinkage performance that is almost identical to that of the highly noxious and environmentally harmful wet chlorine/Hercosett treatment. The company Softal Electronic[6] has developed pilot equipment for APP wool anti-felting treatment.

Size removal has been demonstrated by APP treatments such as helium/oxygen. Thus, for example, PVA can be removed from cotton, albeit at a slow rate, but exposure to APP enables almost complete removal of the size with a cold water wash.

Benefits from the cleaning, activation and etching processes include improved gluing, bonding, coating, printing and lamination with films, enhanced dyeability (increased dyeing kinetics, enhanced depth of shade, improved bath exhaustion) and the ability to carry out post-plasma grafting of actives as a finishing step, e.g. chitosan, keratin, starch, powders, surfactants. Thus, for example:

- Enercon has shown that their 'atmospheric plasma treatment' of PP nonwovens with a helium/oxygen atmosphere results in greatly enhanced adhesion (0% failure tape test) of water-based inks relative to the untreated material (100% failure tape test) and to ambient air corona treatment (10% failure tape test) and delivers superior 'hold-out' of the ink from the nonwoven fibre structure, enhancing depth of colour.

- Controlled atmosphere treatment on spunbond PET nonwovens delivers improved dyeability with water-soluble inks and dyes.[3]
- Softal Electronic's[6] 'Aldyne' APP treatment delivers an adhesive primer monolayer of amine, amide or imide groups, covalently bonded to the uppermost polymer chains of materials such as PP, PE, PET, PVC and PA. Such groups also covalently bond to selected overlayers in, for example, a conversion process putting down inks, coatings or adhesives. The process can completely replace wet priming with its associated high cost and environmental issues.
- PET fabric treated with an APP oxygen process can be grafted with acrylic acid on which chitosan can be immobilised to impart antibacterial properties, resistant to laundering.

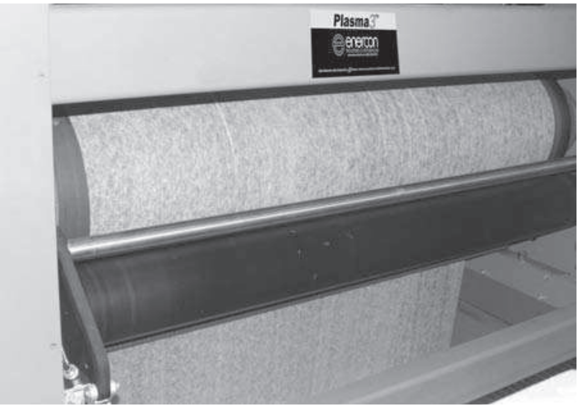
Particular textile segments where controlled atmosphere APP processes are being used include medical industry textiles (gowns, masks, protective clothing), automotive industry textiles (seats, trim, headliners, airbags), apparel industry textiles (outer and under garments), filtration industry textiles (air, water filtration) and flooring industry textiles (carpet fibres).[3]

4.5.3 Gas precursor coating

The gas precursor coating capability is an incremental, but important, advance on the controlled atmosphere treatment. The essential difference is the use of chemically reactive gas precursors which, rather than remaining in the gas state, as with the controlled atmosphere treatment, are polymerised by plasma to form solid phase material. Again, these typically constitute a small percentage of the gas stream with an inert ballast gas comprising the bulk of gas flow. The process proceeds through plasma bombardment of the surface preparing it for coating by activation to create reactive bonding sites. The plasma then deposits molecular fragments and grafts them to the surface while carrying out cross-linking/polymerisation. The single-step APP manufacturing process delivers a dry, fully cured, conformal coating, well-adhered to substrate at individual fibre level. The process is so conformal that each individual fibre accessed by the plasma is coated. The process results in pore-free, uniform thin films with superior, customised physical, chemical, electrical, mechanical and bio-functional properties.

Gas precursor coating is available from, for example, certain Corona systems of Enercon,[3] the Homogeneous DBD systems of Dow Corning Plasma Solutions[2] and the APGD plasma type using the APPJ® technology of APJeT.[11] Figure 4.17 shows a nonwoven under APP processing by Enercon's Plasma3™ system.

Examples of gas precursors and resulting coatings are:



4.17 A nonwoven under APP processing by Enercon's Plasma3^{TM} system. (Courtesy of Enercon Industries Corporation[3].)

- Fluorine-containing gases to give water and stain repellence
- APP polymerisation of organosilicon compounds in the vapour state to impart dielectric properties, thermal stability and scratch resistance. The resulting films can also enhance colour intensity.
- Improved antistatic properties of polyester fabrics by APP grafting and ionisation of acrylic acid and acrylamide vapour precursors.
- APJeT's 'dual functionality' treatment to make a fabric hydrophobic on one side and hydrophilic on the other, without lamination.

4.5.4 Liquid precursor coating

The liquid precursor coating treatment is a step-change advance in surface engineering power and sophistication beyond gas precursor coating similar or greater in magnitude to the difference between controlled atmosphere treatment and ambient air processing. The use of liquid precursors opens up a huge new range of chemical and biological capabilities for APP. The number of potential liquids available to act as precursors runs into hundreds, if not thousands, including as they do, mixtures, dispersions, emulsions, suspensions and colloids, a number far greater than the available gas state precursors. Thus, a particular advantage of liquid precursors is the range of processes available from a single kit. Essentially, by changing the liquid in the delivery system, a totally different process delivering a new surface function is enabled.

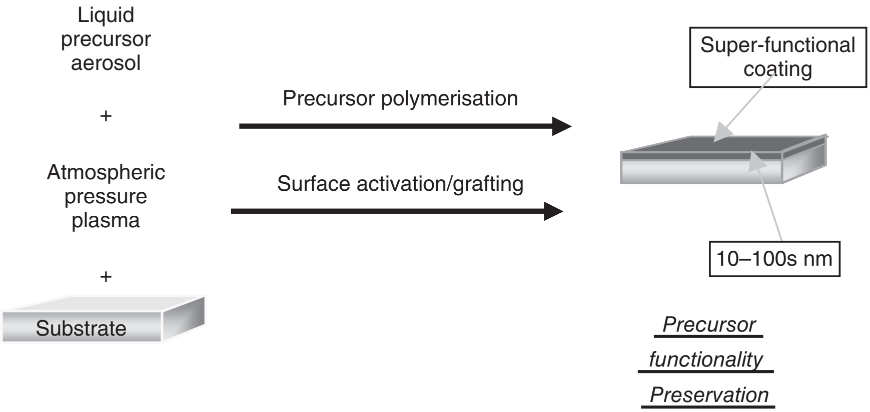
Only two APP manufacturers offer liquid precursor coating equipment: Dow Corning Plasma Solutions of Ireland which uses the homogeneous DBD APP type and Ahlbrandt System GmbH of Germany which uses corona. In both cases, it is the use of coating precursor in its liquid state in the plasma region that defines this APP process. The liquid is not vaporised but is atomised into droplets and injected into the plasma region in the liquid state. It is neither applied before nor after the plasma process since these options do not constitute true liquid precursor coating but mere surface activation plus grafting in the first case and plasma-assisted curing in the second case. The essence of the liquid precursor method is that the coating precursor reaches the plasma in the liquid state.

The Ahlbrandt process is given the acronym 'Wasco' (water–aerosol surface coatings) and takes the form of ~1 µm diameter droplets carried by ballast gas flow into the containment around the corona plasma region. There, a controlled atmosphere corona formed from the ballast gas of nitrogen, argon or, sometimes, ambient air, converts the precursor droplets into a functional coating. The aerosol is generated out of, and limited to, mainly water-based solutions (~85% water) and potential applications include antistatic, adhesion primers and wetting agents. The technology is described in detail elsewhere in this book.

The Dow Corning Plasma Solutions process has the acronym 'APPLD' (atmospheric pressure plasma liquid deposition). Here, the only precursor limitation is the viscosity of the liquid, which must be low enough for the liquid to be readily atomised into droplets ~20–50 µm diameter. Typical viscosity values are ~30 centistokes. Obviously, if the target process involves molecular polymerisation, the precursor molecules must be capable of such, i.e. they must be able to open bonds and engage in cross-linking. The Dow Corning process involves ultrasonic or other nebulisation of the liquid flow and direct injection of the resulting droplet stream into the plasma region. The fabric or fibre is passed through the plasma region containing the droplets and in a single step, the surface is activated and the precursor monomer is polymerised and chemically bonded to the surface to form a functional coating. Figure 4.18 shows this schematically:

A critical result of this process is that the coating preserves the molecular integrity of the original monomer so that its properties and functionality are completely replicated in the coating. There may be a feeling of 'so what' in reading this statement but, in fact, this is a profound and unexpected result. The reason is that conventional plasma processes in all pressure regimes tend to damage or destroy molecules.

As has been argued previously, a large part of the value of a surface engineering treatment is determined by the degree of functionality imparted to the surface by a treatment process. This, typically, in turn, is directly related to the molecular sophistication of the new, treated surface, whether coated, cleaned or activated. This is particularly the case with processes targeting new, advanced textile properties such as bio-functionality and smart textiles. The problem with conventional plasma processes across all pressure regimes is that the degree of surface molecular sophistication



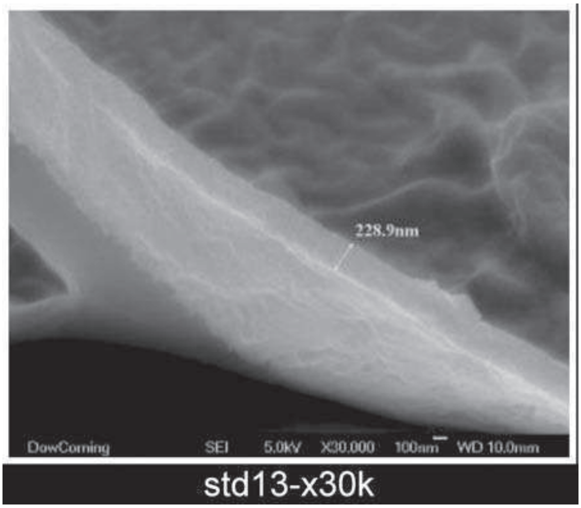
4.18 Schematic of the Dow Corning Plasma Solutions' APPLD Process (Courtesy of Dow Corning Plasma Solutions[2]).

available is severely limited. Thus, conventional plasma-deposited coatings comprise low molecular weight species of limited value or highly specific applicability, e.g. in microelectronics. The obvious solution to the functionality roadblock to product and application diversification is to extend the range of plasma processing. However, this has proven not to be possible with conventional plasma technology due to the highly aggressive nature of the plasma process. Essentially, the plasma destroys at the microscopic level any complex or long-chain molecule injected into the plasma as a precursor of the process. With functionality directly related to the molecular complexity of the precursor, the destruction of complex molecules by conventional plasma has placed a fundamental limit on the functionality of the surface coatings hitherto available to the textile industry and, hence, on its ability to develop new technologies and to find new applications and products.

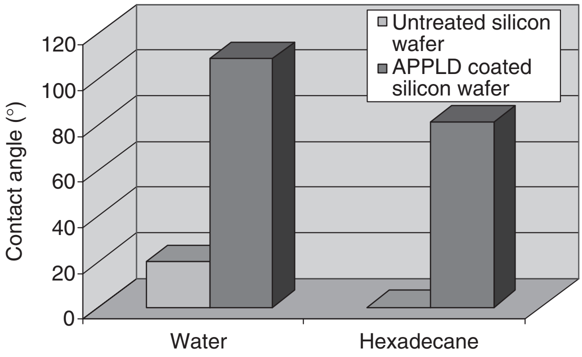
The use of liquid, as opposed to gas or vapour, precursors has removed this functionality roadblock. The original work, sponsored by Dow Corning in the 1990s, found that the precursor within each droplet is protected from the plasma and carried intact to the substrate where it spreads over the surface and is plasma polymerised into a coating. Thus, uniquely using atmospheric pressure plasmas, complex, long-chain and/or fragile precursor molecules with high-level functionality can now be injected into a plasma without being damaged or destroyed. Instead, the plasma causes polymerisation of the precursor so that it is deposited as a conformal, well-adhered thin-film coating, which retains all the functionality and value of the original liquid monomer precursor. Dow Corning calls this process 'controlled polymerisation'. Thus, advanced surface properties can now be made available from controlled polymerisation technology, offering the prospect of plasma processing penetrating a wide range of new, high value textile applications.

Examples of functional coatings that could be achieved by APP liquid precursor coating include:

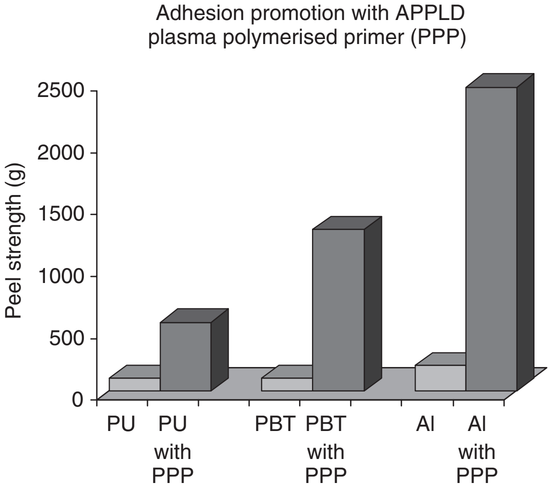
- Hydrophobic coatings for durable, breathable, water repellence, water roll-off and inhibition of capillary flow; dry process for the waterproofing of polyaramid fibres with no loss of fibre strength, e.g. for bulletproof vests.
- Hydrophilic response for water wicking for moisture transferring and quick-drying textiles, e.g. sport, military; extra absorbance, e.g. easy capillary flow; anti-fog; easy take-up and good coverage for painting, coating, dyeing, etc.
- Oleophobic coatings with high oil, solvent, blood, etc. repellence and durability to boiling water and solvent washes (see Figures 4.19 and 4.20)
- Low friction coatings with coefficient of friction comparable to PTFE
- Reactive coatings, e.g. chemically reactive and reagent-specific filtration fabrics
- Non-stick/release – low release force; stain release, e.g. anti-dirt, easy clean workwear, automotive upholstery
- Adhesion promotion coatings for outstanding bondability, coating and lamination (see Figure 4.21)
- Bioactive coatings



4.19 SEM image of an APPLD fluorocarbon coating. (Courtesy of Dow Corning Plasma Solutions[2].)



4.20 Water and hexadecane contact angles from a fluorocarbon APPLD coating. (Courtesy of Dow Corning Plasma Solutions[2].)



4.21 Plasma polymerised primer APPLD coatings give advanced adhesion performance on a range of substrates. Adhesion performance without APPLD primers is shown in lighter grey. (Courtesy of Dow Corning Plasma Solutions[2].)

- ○ Anti-bacterial finishes for both general and medical use – inhibit bacterial growth, achieve reduction in bacteria, e.g. anti-bacterial face masks
- ○ Antifungal finish – inhibit growth of fungi on textiles
- ○ Selective biological tethering sites – bio-receptors/bio-affinity, bio-functional wound dressings
- ○ Grafting of enzymes, proteins, cells

- Copolymers
  - Multifunctional surfaces, e.g. dual function —NH_2 with —COOH groups
  - Smart/responsive surfaces, e.g. F + PEG – in air, stain-repellent F on surface, in water, stain removing PEG on surface
- Trapped active coatings – The coating matrix encapsulates sophisticated active molecules that can be released in a controlled manner over time or through applied stimulus. Potential actives include anti-microbials, enzymes and bio-molecules, pharmaceutical agents, cosmeceuticals, fragrances, agro-chemicals, anti-oxidants, flame retardants, catalysts and photochromic agents.
- Optical coatings
  - Ultraviolet protective textiles – block UV radiation
  - Far infrared textiles – fabric absorbs radiation and re-radiates at lower wavelength to aid body warmth
- Conductive coatings
  - Electromagnetic shielding textiles for medical devices, safety and general uniforms, electronics, assembly equipment, aprons, maternity wear, general wear
  - Antistatic textiles

It should immediately be said that by no means all of the above have been developed as of now (2006), but the precursors exist to make them prospectively a reality. Their realisation or not will be driven by prospective value and market demand. Essentially, APP liquid precursor coating vastly widens the selection of surface functionalities potentially available to the textile manufacturer, thus offering greater choice from a range of design and customisation options, potentially opening the door to new processes, new products and new opportunities.

4.6 The atmospheric-pressure plasma audit

Textile manufacturers everywhere are seeking ways to differentiate themselves from a sea of competition. Atmospheric-pressure plasma surface engineering offers clear advantages when compared to conventional wet chemistry processing. Substrate surfaces can be modified homogeneously in short processing times without any change in bulk properties. A huge range of surface modifications are possible by choosing appropriate plasma types, equipment, and gas or liquid precursors. Chemical consumption is low and the process is safer and much more environmentally friendly. Above all, APP processing, particularly liquid precursor coating treatments, offers the textile industry extensive potential for innovation and more flexible manufacturing capabilities.

For all that, APP processing is only beginning to emerge into textile manufacturing and it is instructive to return to the start of this chapter to the set of criteria for the introduction of new technology into the textile market and to try to audit APP processing against such.

'Qualifier' criteria for new textile technologies were listed as:

- Safety and handling: *The new technology must be operated safely, predominantly needing only the existing skill set of the textile mills.* The only issue here is that APP operation requires a new skill set and the training or hiring of skilled operators. However, this is not seen as a significant barrier.
- Operating speed: *Line speeds need to be as fast as or faster than existing technologies to avoid bottlenecks.* Whether or not this is an issue is entirely process dependent. In some cases, APP treatment runs slower than target line speed but in many cases it does not and APP line speeds are rising constantly.
- Production flexibility: *Fast switching between fabric types and effects must be available to allow for rapid adaptations in product and process.* The flexibility of APP is totally equipment specific. Ambient air Corona is a single fixed process but the process options increase rapidly as you move through controlled atmosphere treatment to the gas and liquid precursor coatings. As previously said, the liquid precursor coating systems offer hundreds of potential processes from one kit.
- Investment: *The technology should offer a return on investment in under 5 years and maintain or improve the profitability of the mill.* This can only be assessed on a case-by-case basis. In specific cases where APP is up and running in textile mills, the evidence is clear, APP can and does meet this criterion. In other cases involving the introduction of new effects using new APP technology, the case has not yet been made.
- Environmental: *The technology should comply with existing legislation and improve compatibility with anticipated law.* This is where APP undoubtedly scores with proven massive superiority over wet and heat based processing in terms of environmental impact.

'Winner' criteria for new technology in textiles were characterised as:

- New effects: *Properties and performances not achievable by traditional technologies enabling added value and market differentiation.* This is a real driver for APP, particularly for the APP coating technologies, whether single-step coating or grafting following APP activation. There is no doubt that plasma-deposited functional coatings are now offering interesting prospective new textile properties and performances for technical and apparel applications. These range from embedded scents, stay-clean fabrics and fabrics with anti-bacterial action to coatings which exude insect repellents or pharmacological or other therapies. However, the issue, as always, is value vs. cost and it is at present unclear whether all of the relevant APP technology is sufficiently advanced in terms of manufacturability to deliver solutions of commercial interest. Undoubtedly, developing technology will cross that threshold in the foreseeable future to access a range of high-value specialty products that will expand into high volume markets.

- Durability: *Significantly exceeds the durability of effects delivered by current processing techniques, again adding value and distinction.* Durability is highly process dependant and many APP processes do not deliver the same level of durability to laundering, etc. as wet coatings. A major reason is the thinness of plasma coatings which can be <1/20th that of wet coatings. However, in many applications, such as single-use medical fabric, this is not an issue and even where it is an issue, APP coatings are rapidly improving in performance to become competitive with wet coatings.
- Operating costs: *Costs should be substantially reduced relative to established manufacturing norms facilitating competitive pricing and/or profitability improvements.* There are many examples of both capital and running cost reduction through adoption of APP. Thus, for example, the company Softal Electronic[6] claims a payback time of only 9 months single-shift operation for its Aldyne plasma adhesion primer system versus conventional liquid priming, with savings of over €3 million in 60 months use. There is no doubt that, as the costs of raw materials, power and water continue to rise steeply, the underlying cost advantages of APP over wet processing in terms of zero to low chemicals consumption, low power need and very low water usage will motivate textile manufacturers to move to APP wherever feasible.
- Environmental: *Sets new industry benchmark.* As stated, this is an area in which APP scores massively in comparison to any other competing textile processing technology. This criterion is undoubtedly a winner for APP processing, which is setting new industry benchmarks.

APP changes the surface of textiles. It can replace current wet- and heat-based processing to reduce direct costs and to reduce or even eliminate harm to the environment. It can deliver new effects. It can provide winners for daring textile manufacturers. However, it is only in recent years emerging onto the textile manufacturing scene as a serious option and beginning to prove itself as a candidate for mainstream processing. Much has been done by the partnership of the textile industry and the plasma processing provider community, but much remains to do. To this end, both partners need to work closely together and have the courage and foresight to implement a long-term strategy of sustained investment in plasma technology.

Global environmental issues alone motivate such a strategy and should encourage significant support from national and supra-national bodies such as the European Union and the US Federal Government.

Already in the marketplace are mature APP technologies with well-defined technical capabilities serving both new and mature markets. These are enjoying steady growth driven by need to replace non-sustainable processing and reduce costs. More speculative but potentially more exciting are emerging APP technologies such as gas and liquid deposition, where relatively high costs must be justified by high added value so that these technologies must seek new, high value markets, in particular technical textiles from which they can launch drives into major volume markets.

There is no 'superior' APP technology. The textile producer has a range of value/cost options increasingly provided by the APP community and needs to select the APP product that exactly delivers the required level of surface functionalisation, manufacturability and commercial performances at the lowest cost and highest margin to him/her.

Driven by a crazily burgeoning global population with all its adverse consequences in terms of sustainability and driven also by the insatiable human need for enhanced performance in every measurable parameter such as comfort, safety and function, there is little doubt that atmospheric-pressure plasmas stand on the threshold of a revolution in textile processing as great as that delivered by wet- and heat-based processing in times long past.

We do, indeed, live in interesting times.

4.7 References

1. Plasmatreat GmbH www.plasmatreat.de.
2. Dow Corning Plasma Solutions www.dowcorning.com/plasma/. Dow Corning Plasma Solutions is a Registered Business Name and the trading name of Dow Corning Ireland Limited.
3. Enercon Industries Corporation www.enerconind.com.
4. Vetaphone A/s www.vetaphone.com.
5. Ahlbrandt System GmbH www.ahlbrandt.de.
6. Softal Electronic www.softal.de.
7. Pillar Technologies www.pillartech.com.
8. AFS Entwicklungs- und Vertriebs GmbH www.afs.biz.
9. Sigma Technologies International, Inc. www.sigmalabs.com.
10. Air Products & Chemicals, Inc. www.airproducts.com.
11. APJet, Inc. www.apjet.com.

5

Corona and dielectric barrier discharge plasma treatment of textiles for technical applications

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5.1 Introduction to atmospheric-pressure plasma processes

Growing demands on the functionality of technical textiles as well as on the environmental friendliness of finishing processes increase the interest in physically induced techniques for surface modification and coating of textiles. In general, after the application of water-based finishing systems, the textile needs to be dried. The removing of water is energy intensive and therefore expensive. In contrast to conventional wet finishing processes, a plasma treatment is a dry process. The textile stays dry and, accordingly, drying processes can be avoided and no waste water occurs. Plasma treatments represent, therefore, energy efficient and economic alternatives to classical textile finishing processes. Within plasma processes, a high reactive gaseous phase interacts with the surface of a substrate. In principle, all polymeric and natural fibres can be plasma treated.

For many years, mainly low-pressure plasma processes have been developed for textile plasma treatment. However, the integration of these processes, which typically run at pressures between 0.1 and 1 mbar, into continuously and often fast-running textile production and finishing lines is complex or even impossible. In addition, due to the need for vacuum technology, low-pressure processes are expensive.

The reasons why plasma processes at atmospheric pressure are advantageous for the textile industry are in detail:

- The typical working width of textile machines is between 1.5 and 10 meters. Textile-suited plasma modules need to be scalable up to these dimensions, which is easier for atmospheric-pressure techniques.
- Textiles have large specific surfaces compared to foils, piece goods or bulk solids. Even with strong pumps, the reduced pressure which is necessary for low pressure plasma will only be reached slowly due to the desorption of adsorbed gases.

- Depending on the fibre material, textiles can adsorb and absorb relatively large amounts of water. To reduce the chamber pressure below the vapor pressure of water (23.4 mbar at 20 °C), a drying process is necessary. This is time consuming because diffusion processes within the fiber and the cooling due to evaporation of the water slow down the drying (vapour pressure of ice: 4.02 mbar at –5 °C). The evaporation time can be shortened by heating the substrate.
- Atmospheric-pressure processes can be combined with spraying or aqueous aerosols.
- Atmospheric-pressure processes are in-line capable, in contrast to batch low-pressure plasma processes.
- Investment and maintenance costs for atmospheric-pressure plasma modules are moderate.

New markets can be opened if plasma processes that have been developed for low-pressure conditions so far are transferred to normal pressure conditions.[1] The dielectric barrier discharge (DBD) process belongs to those plasma processes that can also be applied at atmospheric pressure. Therefore, research efforts are being made over many years, with cooperation between partners from textile and plasma research institutes and industry, in order to make DBD technology a useful and practicable method for the textile industry, aiming at the development of new products, improved textile functions and sustainable processes.[2,3]

A focus of ITV Denkendorf, within its research and development projects, are new technologies for continuous plasma coating of wide fabrics under atmospheric pressure and the improvement of the profitability of the plasma coating processes. For example, oil and water repellent layers are deposited on the substrate and new processes are opened up by combining plasma treatments with sprayed aerosols.

Only low-temperature discharges can be used in order to functionalise textiles by plasma treatment.[4] In low-temperature plasmas, the thermal energy of the neutral atoms and molecules stay roughly at room temperature; however, the free electrons can transmit high energy. So the electrons have to be heated to a minimum of 10 000 K, while the gas temperature, which is controlled by the thermal energy of atoms and molecules, remains at moderate temperatures. These plasmas can interact with the polymer surface for some milliseconds without thermally changing the substrate. In thermal plasmas, however, the neutral particles are in thermal equilibrium with the charged particles and transmit too much energy to the polymer surface, which instantly destroys the textile. Flame treatment as thermal plasma is common in textile processing; however, this technology is mainly used for the removing of the hairs of textiles – not for functionalisation.

Functionalising is a chemical process. Thereby, the reaction time of the reaction partner is an important process parameter. This means for a plasma treatment, the longer the polymer surface is exposed to the activated reactive gas, the more functional groups are formed, and within limits the better is the desired effect.

5.1.1 Corona discharge

In material processing practice, the term ‘corona discharge’ is often understood differently from the term in physics and electronics. Strictly speaking, corona discharge occurs if a rather asymmetrical electric field has an effect in a gas causing electric current to flow in a range between μA and mA. The considerable inhomogeneous field needed for this is typically reached by an asymmetrical shaping of the electrodes. The simplest electrode configuration consists of a metallic needle opposite a conductive plate, or of a thin wire within a metallic cylinder.

If the metallic needle or the wire, respectively, is connected to the negative pole of a power supply and the large, extensive electrode (plate and cylinder, respectively) is connected to the positive pole, a negative corona discharge occurs. In the reverse case of polarity, a positive corona discharge is the result.[5] Corona discharge differs from glow discharge (weak current) and arc discharge (high current) with respect to the flow of current. Within a corona discharge, the current varies over a wide range and is mainly caused by charge carriers of only one polarity. The electric field mainly concentrates at the highly curved electrodes. Therefore, light emissions occur in a negative corona at this cathode region. Most of the gap between the electrodes remains dark, however. This so-called ‘drift zone’ is occupied by negatively charged particles. In this area, the charge carriers are decelerated by permanent collisions between the gas particles and slowly drift towards the electrode. In the glowing region of high electric field strength, the charge carriers can receive enough kinetic energy between two collisions with gas particles to transmit sufficient energy to fragmentise, ionise or set the collision partners in strong molecular vibration. If electrons are excited by the collision to energetically higher states, light quantums can be emitted when the electrons reoccupy the lower energy level.

In the case of a negative corona, electrons are generated in the strong electrical field at the curved electrode. These electrons are accelerated within the field and transfer their energy to surrounding gas particles. Subsequently, they are taken up by neutral particles in the dark drifting zone and form negative ions, which slowly drift towards the large and positively charged anode.

In the case of a positive corona, no electrons can be set free at the cathode. In the drifting zone the electric current is practically carried only by positive charge carriers. When they impinge on the cathode, they cannot – in contrast to the negative corona – eject new electrons from the electrode. Negative charge carriers in the drifting zone can be generated only by photoionisation or natural radioactivity. These can only cumulatively multiply in the area of very high field strength near to the positively charged, needle-like electrode. Under similar external conditions, the positive corona discharge is inhibited, in contrast to the negative corona discharge. The discharge current is halved.

The typical field strengths for corona discharges are roughly around 40 and 50 kV/cm at radii between 2 and 10 mm. Discharge currents range between μA and mA. A typical corona discharge current is below 200 μA.[6]

Such 'real' corona discharges are used for textile treatment in order to either remove or to specifically apply electrostatic surface charges from or to fabric layers, but not for surface functionalisation or activation. The electrostatic discharge of fabric layers is, for example, advantageous in the case of hydrophobic fibres such as PP-nonwovens or textiles finished with fluorocarbons. Due to friction and contact with non-grounded surfaces, surface charges can occur which exert strong, long-reaching coulomb forces on fabrics, thus, for example, preventing proper plaiting. The charged fabric, moreover, tends to attract dust particles. Normally, dust is not quite neutral but slightly negatively charged so that dust particles whirled up by air flows are directed to the textile surface by positive charges and adhere due to electrostatic forces. If the fabric layer is discharged, the dust particles can be sucked off. In the textile industry, re-damping by aerosols is improved by electrostatic charge.[7] Textile webs and yarns with the same electric charges repel each other, thus avoiding blocking.

In the case of fabrics and webs processed at high velocities, a gas boundary layer is coupled to the surface. Corona discharge helps to convert this layer from a laminar to a turbulent flow. This facilitates the drying process of the web as the steam is transported, along with the fabric, in the laminar boundary layer. As a turbulent flow, the humid layer can more effectively be sucked off from the fabric.[8,9] The prerequisite for switching a flow from laminar to turbulent, however, is that the flow is already relatively close to instability. This means that the discharge process is not able to cause any turbulence over slowly moving surfaces. This technology is distributed by the company Eltex (EFD-technology). Corona discharge can further be used in order to effectively exchange the air entrapped within a textile and to substitute it by inert or reactive gas. It has been shown that the efficiency in the discharge-supported exchange of oxygen by nitrogen within a fast running web increases with the web velocity. Sixty-three per cent of the entrapped oxygen was washed out by nitrogen at 55 m/min web speed, whereas at 150 m/min web velocity, 86% of the entrapped oxygen was exchanged by nitrogen.[10,11]

5.1.2 Dielectric barrier discharge

The set-up for dielectric barrier discharge processes, although similar to the corona discharge, has characteristic deviations from the corona set-up. The most important characteristic is that at least one electrode is coated completely by an insulator, the dielectric barrier for electric currents.

The Dielectric Barrier Discharge (DBD) belongs to the class of non-equilibrium low-temperature plasmas. The DBD is characterised by high energy of the free electrons, while the ions and neutral particles gain only little additional kinetic energy. Kinetic energy and momentum is transferred to the particles upon collision with electrons which have been accelerated along the electric field lines. Because of their low weight and small collision cross-section, the electrons gain considerably more thermal energy compared to the heavy and large gas particles. Upon collision between the fast electrons and gas molecules or atoms, the molecules are fragmented or transferred into electronically excited highly reactive states.

The formation of a dielectric barrier discharge process is complex and will be described only in basic detail here. First an electric field is created. Free charge carriers are accelerated by coulomb forces in this field. Even a very few free electrons from a natural source such as cosmic radiation or natural radioactivity are sufficient to initiate a discharge process. These charge carriers are accelerated within the field and generate new ion-electron-pairs upon collision with neutral gas particles. Mainly the light electrons are accelerated and absorb thermal energy. Additional electrons are emitted into the gas gap upon the impact of ions on the electrode. The avalanche-like generated cloud of charge carrier moves towards the positively charged electrode. The characteristic light emissions within the visible and UV-range of plasma discharges result from collision-induced electronically excited states of the gas atoms and molecules. The electric field between the counter electrode and the charged cloud becomes stronger, while the field between the negatively charged electrode and the cloud breaks down. At the time the electron cloud reaches the positively charged electrode, the complete high voltage is applied at the dielectric electrode coating and the gas gap is field-free. No currents can flow any longer and the discharge is extinguished, although the whole gas gap is still electrically conductive. This breakdown process of initiation, avalanche-like charge carrier generation, and extinguishing happens within a few nanoseconds. However, dependencies with the kind of gas, gas gap size, gas pressure and nature of the dielectric coating exist.

The DBD is so-called ‘filamented’. At normal pressure, many single-discharge filaments, also called streamers, are generated within the gap between the electrodes in spatial and temporal random distribution over the length of the gap. The individual discharge filaments do not interact with each other apart from the initial electron generation by UV-radiation. One filament has a radius of around 0.1 mm and transports an average electric current of 0.1 A. The average electron energy ranges between 1 and 10 eV. The dissipated amount of energy per filament is in the range of microjoules. A discharge that hits the dielectric layer of the counter electrode generates a so-called footprint – an area where the charge is distributed on the dielectric surface by sliding discharges. The footprint is a few square millimetres in size and is considerably larger than the discharge filament diameter.[12–14] These surface discharges also occur on the surfaces of textile fibres, which are located within the discharge gap. These surface discharges enhance the effect of the DBD with respect to a fibre surface functionalisation because reactive species are generated exactly at the fibre surface where they are needed for the reaction process.

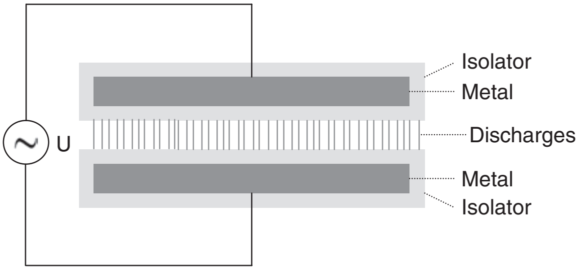
Dielectric barrier discharge is the most commonly applied technology in order to achieve an easily up-scalable, expanded, non-equilibrium plasma for the treatment of wide webs and fabrics. The free electrons in the plasma discharge are heated up to 10 000–100 000 K while the gas itself can be kept at moderate temperatures, typically between room temperature and 100 °C. This allows the treatment of textiles without thermal damaging of the fibrous substrate. The ambient air is often used as a process gas in a DBD because of its easy availability and the reactivity of the oxygen. The molecular oxygen in the air can be converted into reactive atomic oxygen radicals or excited ozone molecules.

The set-up for DBD processes is typically characterised by the combination of two opposing electrodes with an intermediate mm-sized air gap. At least one electrode is coated by an insulator. The dielectric barrier covers the whole surface of the electrode and acts as an isolating barrier for electric currents. The dielectric layer needs to be resistant to high voltages of a few kV. It has to suppress electric currents even when the high voltage is applied. Only negligible currents through the barrier are allowed. Local avalanche breakdowns through the barrier may not occur. The electrode arrangement of the barrier discharge acts like several condensers in series, with different capacities and dielectric strengths, within an electric circuit. The gas gap forms the condenser, which leads to the avalanche breakdown within the gap when a sufficiently high voltage is applied. A spark develops and the condenser is temporarily discharged, caused by the electrically conductive plasma. The electric current which flows during the discharge is obstructed by collisions with and between gas particles. The gas forms a resistor, which transfers energy into the gas. The dielectric coatings of the electrodes inhibit an uncontrolled current such as an arc discharge between the electrodes. Only alternating currents can pass the condenser while direct currents are blocked. In order to repeatedly or almost continuously couple power to the discharge, a DBD must be run with alternating currents. A second discharge at the same site can only take place when either the voltage has been doubled or when the polarity sign has been inverted. The common frequencies range between 1 and 100 kHz. The excitation frequency depends on the resonance frequency of the oscillating circuit, which is formed by the transformer coil, electrode gap and dielectrics. Relatively high power can be coupled to the plasma if frequencies are excited that are close to the resonance frequency. Frequencies that deviate significantly from the resonance frequency can couple only little power into the system.

At the minimum ignition voltage, the discharge ignites only at an especially favourable point. If the electrodes, for example, are not quite plane-parallel to each other, the site with the smallest gap is the preferred site for the first discharge. If the voltage is increased, more discharges are generated side-by-side at other sites, which fill the whole gap between the electrodes with a discontinuous plasma.

The technical term dielectric barrier discharge has been established in the textile and foil processing industries for the above-described processes. However, in practice, processes with discharge by commonly only one dielectric layer and preferably in air are also often called corona discharge. This is technically speaking not correct, because dielectric barrier discharges fundamentally differ from corona discharges. Both, corona discharges and DBD are so-called silent discharges but in contrast to the DBD, corona discharges have an extensive dark field and are generated between two highly asymmetrically formed metallic electrodes. The coating of at least one of the two electrodes by a high-resistant dielectric barrier practically prevents the operation under conditions of direct current. At corona arrangements, low-resistant barriers can prevent an arc discharge and distribute direct current equally to many point electrodes. The electrical current at each electrode is quite often limited by an inserted protective resistor. In dielectric barrier discharge, however, highly-resistant coatings such as glass, ceramics or silicone rubber (PDMS) are used, whose electrical conductivity can practically be neglected. The total high voltage must be applicable to the barrier layer without leading to avalanche break-down events.

One reason for the misuse of the corona term is that, in many cases, a considerably asymmetrical electrode configuration is chosen for barrier discharges of fabrics or foils. The fabric is directed over a broad roller which forms one often grounded electrode. The high-voltage bar-shaped electrodes are arranged around the roller, parallel to the roller axis; however, they are small compared to the radius of the roller. This results in the following definition of dielectric barrier discharge DBD:



5.1 Principle of dielectric barrier discharge.

A dielectric barrier discharge (DBD) is a filamented discharge between two electrodes with at least one dielectric, with a high frequency excitation, mostly in the range between 1 and 100 kHz (Fig. 5.1).

The traditional and most common application of corona and DBD technology, respectively, is the improvement of wetting of non-polar surfaces. Such low-energy surfaces, which are typical for polymeric materials, have poor wetting properties with regard to polar, high surface tension liquids. A high surface tension liquid such as water or water-based dispersion only spreads and forms a stable film on surfaces with comparable high surface tension. On non-polar, polymeric surfaces, aqueous films will break and dewet, forming single, isolated droplets. A stable film formation is important for printing, varnishing, coating and several other applications. DBD treatment often helps to avoid these dewetting phenomena by increasing the surface energy. The advantages of DBD treatment are better wetting and better adhesion of the printed dyestuff or lacquer to the treated substrate. This positive effect of DBD treatment is also used in combination with glue. Hot-melt, reactive adhesive and water-based adhesive layers have an improved peel adhesion on plasma functionalised polymers.

The DBD process is especially of use for applications with roll-to-roll systems with thermally sensitive materials such as foil, textiles or photographic print paper. But DBD is used to alter other materials such as wood, insulated cable or even fingernails. The benefits of DBD with regard to technical textiles are described in more detail later.

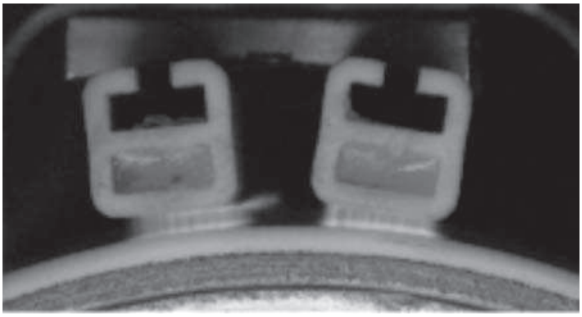
5.2 Special adaptations of DBD technology to textiles

The potential of surface modification of roll goods by corona discharge technology has been known for a long time and has been established in areas such as the foil industry.[15] However, attempts to use the same technology for textile treatment usually failed.[16] This is because the corona treatment of foils has been usually performed with a set-up of metallic electrodes. A polymeric foil, though usually a non-porous electrical insulator, then acts as a dielectric barrier between the electrodes. The foil forms either a dielectric barrier on one electrode if it is in tight contact to the electrode and the discharge filament end is on the surface of the foil, or two separate discharges occur if there are gaps between the foil and both electrodes. Thus, a corona treatment of foils has, in effect, many characteristics of a dielectric barrier discharge. Problems with the corona treatment of textiles occur because textiles differ from foils in many aspects – textiles are commonly thicker than foils and have an inhomogeneous structure. They are porous and gas permeable and typically very rough, even hairy. Their specific surface area is much larger than those of foils. Therefore, textiles cannot inhibit the penetration of the discharge as do foils. Discharge streamers can pass through the textile along the electric field direction, at least locally. These filaments are high-current, hot discharge streamers because the gap between the electrode has to be wide according to the thickness of the textile and no dielectric barrier on the electrodes limits the current in the corona set-up. The high current flow along the yarn surface through the textile can induce carbonisation of the polymer. Even minimal carbonisation increases the local electrical conductivity of the substrate permanently. This, however, results in a subsequent concentration and localisation of further discharges at this point, damaging the textile increasingly. The typical results are micro-fine holes within the substrate.

In paper finishing, this effect of micro-perforation is partly used in order to generate specific properties such as improved air permeability or different filtering behaviour.[17] Textiles, however, are considerably more inhomogeneous than paper and it is hardly possible to control the process towards well-directed perforation via corona discharges.

Since textile perforation is commonly an undesired result, the aim of textile plasma treatment is to achieve a discharge that is as homogeneous as possible. The surface functionalisation should take place as effectively as possible and be as gentle as possible for the substrate. This aim can be reached by different modifications to the established corona technology. Several combinations of metal, silicone-, glass- and ceramic-coated electrodes have already been tested for the treatment of textiles. It turned out that the use of only one dielectric – as it is meanwhile common for foil treatment with a dielectric-coated roller – is not sufficient for the treatment of textiles. Textiles can be better treated by means of two dielectric-coated electrodes. This is because, via two dielectric barriers, the electric current distributes into more single filament discharges thus making the discharge pattern more homogenous (Figure 5.2).[9]

It is further recommended to select a discharge gap as narrow as possible. This is because, with increasing distance, the breakdown voltage rises and the size of the footprints as well as the current of a single discharge increases. High local currents, however, can damage the textile. Accordingly,



5.2 Dielectric barrier discharge between ceramic-coated electrodes.

voltage must be adapted to the dimension of the discharge gap and the textile to be treated. So, the shorter the electrode distance, the lower is the necessary breakdown voltage and the lower is the current in the single filament. A narrow gap facilitates a homogeneous coupling of power to the discharge.

It is further found that textiles usually need to be treated at much lower substrate velocity than foils to gain comparable and satisfactory results. This is because textiles have a much larger specific surface than foils, due to their fibrous structure. In order to generate a surface density of functional groups comparable to foils, it is necessary to generate considerably more reactive sites. Furthermore, in textiles, the filaments of a yarn are closely packed, thus obstructing the exchange of gases. Therefore, textiles must be exposed to a plasma for a longer time compared with foils, in order to compensate both disadvantages, the large surface area and the reduced accessibility of the activated plasma gases to the fibre surface. This can be best attained by reducing the fabric-speed or by scale-up, arranging more electrodes in sequence.

Modifications of the electrode configuration are helpful as well. A more symmetric electrode assembly is advantageous for textile treatment. This is because an equal number of discharge filaments is generated during each half wave of the alternating potential of the electrodes when the electrodes are symmetrically assembled. Each discharge in each direction during each half wave carries approximately the same current, enhancing the overall homogeneity of the discharge.

Intermitting of the excitation frequency is another suitable tool to make the DBD more homogeneous. Intermittation means to electronically switch the generator on and off according to a given pulse-break ratio. This enables one to control the coupling of power independently of the applied voltage. Intermitting mode can be of further advantage for rather slow plasma activated reactions. Reactive gases, e.g. for plasma polymerisation, can be fed into the plasma zone during a break. Chemical processes can continue during the break, thus saving unnecessary energy.

The results of DBD treatments of textiles from natural fibres, e.g. wool or cotton, and also man-made fibres, have been frequently published. Significant changes of textile properties such as friction coefficient, surface energy or improved antistatic behaviour have been reported.[5–7]

5.2.1 Principal chemical processes in DBD systems and aspects of heating

The chemical processes that are initiated in the plasma are usually very complex and depend on the chemical species in the gas gap. In synthetic air alone ($O_2 + N_2$), more than 100 reaction paths and some 30 different species must be considered in order to understand the processes within a DBD. The gaseous molecules are excited and partially fragmented ready to react with a partner in a chemical reaction. Positive ions are generated upon collision with high energy electrons, whereas the capture of slow electrons leads to the formation of negatively charged ions. These charge carriers, however, are only short-lived and disappear within approximately 50 ns after the initialisation of the discharge process.

Nitrogen and oxygen, as main components of air, are the most important collision partners of the accelerated electrons, if the DBD is performed with air as plasma gas. Generated neutral radicals such as $O(^3P)$ and $O(^1D)$ as well as $N(^4S)$ and $N(D)$ react with surface molecules or with molecular oxygen in different electronic states O_2, $O_2(A)$, $O_2(a)$, $O_2(b)$ and nitrogen N_2, $N_2(A)$ to more stable intermediate products such as O_3^* or NO or NO_2. The excited ozone disappears after approximately one millisecond, while stable ozone remains. Nitrogen monoxide is converted after the discharge into different nitrogen oxides – N_2O, N_2O_5, N_2O_3 and NO_3 – within the tenth of a second.[9] Hazardous gases such as ozone, which are typically generated within a DBD in air, need to be exhausted, disposed of or destroyed, e.g. with activated carbon filters, in order to guarantee workplace safety.

In order to generate a streamer discharge in air, the breakdown field strength of 27 kV/cm must be exceeded. The actual voltage to be applied also depends on the nature of the dielectric barrier.

Apart from oxygen and nitrogen, real air does also contain water, CO_2, hydrogen and rare gases, all of which are involved in the reaction mechanisms. Rare gases such as argon, however, are not really inert in a plasma, because they can transfer energy and even be converted into short-lived, energy-rich molecules, so-called ‘excimers’.

Although the DBD is a so-called ‘cold discharge’, the electrodes will become hot with time. A control over the electrode temperature by cooling of the electrodes can be necessary for different reasons:

- First, after a typical DBD-treatment over several hours, the temperature of the electrodes will rise to between 100 and 200 °C. The textile properties are likely to be changed by thermal stress. Textiles which remove heat insufficiently, e.g. due to low web speed, can display increased brittleness or changed colour.
- Second, plasma processes are temperature dependent. If, for example, a polymer layer is to be deposited in the plasma, heat might impede the polymerisation and deposition. On the other hand, moderately heated electrodes can support a hydrophilic treatment of textiles in air. A plasma regime change can be observed in air when the temperature approaches 80–100 °C. In the case of hot electrodes, the discharge is more homogeneous and less filamented than with cold electrodes. The coupled power decreases measurably switching from cold to hot electrodes, while the voltage remains constant. It is supposed that the change of the plasma regime goes along with the stability of ozone; the plasma generated ozone becomes unstable when the temperatures exceed 80 °C. It is assumed that it is mainly the enforced decay of ozone that causes the observed regime change. More oxygen atoms are generated, which are available for the surface modification, thus accelerating the process to impart hydrophilic properties to the fabric.

The aim, therefore, is an efficient adjustment of temperature and cooling of the system to achieve optimal treatment results for continuous DBD operation. This can be efficiently reached by cooling the electrodes.

5.2.2 Technical possibilities of DBD technology

Fabrics such as woven fabrics, knitted and warp knits, nonwovens, laid fabrics, papers and foils, as well as mono and multifilaments, staple fibre yarns, roving yarn, carded nonwovens but also single fibres and powders, can be treated with the described method of dielectric barrier discharge. Limitations or specific configurations are, for example, necessary for electrically conductive textiles. In a common DBD set-up, the endless substrate should be an electric insulator. Otherwise it is likely that electric currents flow along the substrate to the grounded parts of the machine that it is in contact with, such as grounded deflection rollers. High current discharges between the textile and the grounded element might occur, which might damage the substrate.

A specific tandem DBD set-up has been described to treat electrically conductive substrates potential-free. The set-up consists of two symmetrically arranged pairs of electrodes. They are electrically controlled in a way that a filament-like discharge occurs between the first electrode and the substrate. The discharge current flows along the substrate to the second discharge zone. The filamented discharge at this plasma zone closes the electric circuit.[18]

5.3 Plasma-induced surface activation of fibres

Plasma surface activation is usually understood as a plasma treatment under non-polymerising conditions. The chemical surface modification is initiated by radical reactions of the plasma-activated gases or plasma-generated UV-irradiation without a layer deposition. In atmospheric pressure plasmas, the surface activation typically takes place with oxygen-containing gas mixtures such as air. Surfaces with low functionality become more reactive by enhancing the concentration of oxygen-containing or other polar groups at the surface. Activation can also mean the increased wettability of surfaces whose surface energy is increased by the polar surface groups.[19] Surface energy is an important characteristic value, especially for wettability by aqueous systems.

5.3.1 Applications of DBD treatment in technical textiles

For many, particularly technical, applications of the textiles, strong adhesive bonds between the textiles and other substrates are needed. Thus, bonding, coating or laminating are important working steps. They are responsible for efficient processing and sustainable functionality of the product. Problems in the assurance of durable adhesion to textile substrates have many causes. The flexibility of a textile poses a specific challenge for adhesive bonds. On the fibers, residues from processing agents like spin finish or sizing agent, which originate from the previous manufacturing steps, prevent good adhesion to fibre surfaces. But even a pure surface of a synthetic fibre such as polyester (PET), polyacrylonitrile (PAN) or highly drawn polyolefine has a crystalline and hydrophobic character. Wettability and chemical reactivity of synthetic fibres are therefore usually poor and adhesion forces are weak.

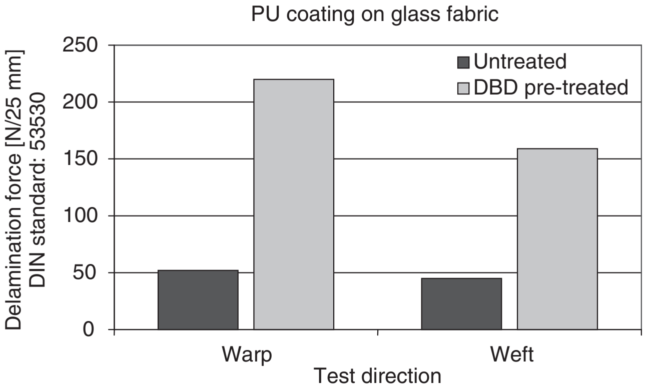
In the following, the potential of DBD treatments to improve the adhesion of coatings and bondings to other substrates will be demonstrated by practical examples. In all cases, the subsequent processing of the plasma-treated textiles has taken place following a period of at least a few hours after the DBD treatment. This evaluates the practicability of the process because it has to be tolerant to short storage times and typical delays in the manufacturing process. Due to this waiting period, it is assumed that, at the time of processing of the plasma treated textiles, no short-lived reactive functions such as unsaturated radicals exist any more on the fibre, but polar, oxygen-containing groups are the basis for the observed adhesion effects.

For the practical tests, mainly polyurethane coatings were applied to different textile substrates. Due to their elastic and film-forming properties, polyurethanes are an important material class for coating and bonding of textiles. Although solvent-based polyurethanes are still processed in a few instances, in most cases water-based polyurethane dispersions are used. An improved wetting of the textiles by these dispersions should result in improved adhesion. For example, DBD-treated and non-treated polyester fabrics have been PU-coated using a water-based polyurethane dispersion. After drying and curing, the delamination force, measured by peel tests, was found to be 50–200% higher on the plasma pre-treated than on the non-activated fabric, depending on the dose.

As a second example, two polyester fabrics have been bonded to each other by a direct processed polyurethane film. Peel tests proved that the adhesion force could be enhanced many times over a non-activated sample by plasma pre-treatment, depending on plasma dose.

A DBD pre-treatment significantly improved, even with glass fabrics, the adhesion of a polyurethane coating that was applied by transfer coating. For both warp and weft direction, the delamination forces of the coating increased by a few hundred per cent (Figure 5.3). In addition to the better adhesion performance, the plasma pre-treated material was much more resistant to hydrolysis than the non-activated fabric and, even after 90 days of immersion in water only few signs of delamination could be found.

DBD pre-treatment is not only effective with regard to water-based coatings and glues. For example, co-polyamide hot-melts were coated onto a polyester multifilament fabric at a critical low processing temperature, with usually poor resultant adhesion performance as measured by a peel test according to DIN 53357. As another example, to improve the adhesion of a seam-sealing tape, the top charmeuse layer of a three-layer laminate for



5.3 Enhanced adhesion performance of coatings by plasma activation of the fabric.

functional clothing was DBD pre-treated. The adhesion force of the tape was measured by a peel test according to DIN 53530. In both cases, the hot-melt and the tape, the adhesion force was found to be doubled compared with non-pre-treated fabrics.

Other applications of plasma activation of textiles have enhanced water pick-up and intensified and improved dying results with pre-treated textiles.

5.3.2 Mechanism of surface activation

Important steps during an air-plasma treatment of polymers are exemplarily described below for polyethylene. A carbon–hydrogen bond gets cleaved by either electron impact, photo effect or energy transfer from an excited atom or molecule. The released hydrogen radical is removed by diffusion or chemical reaction. A single occupied unstable and high reactive sp^3-orbital remains at the carbon atom. This radical site can react fast with an oxygen molecule, forming a peroxy radical. Alternatively, the secondary radical can be stabilised by additional hydrogen separation in the neighbourhood, resulting in carbon–carbon double bonds or stable allyl radicals. The fast reaction of the alkyl radical with oxygen is preferred with regard to a possible reaction with nitrogen because oxygen molecules have a radical character. The generated peroxy radical at the polymer chain can be transferred into a hydroperoxy function by separating a hydrogen atom from a neighbouring carbon atom. This can initiate a chain reaction because the newly generated radical can react with an oxygen molecule on its part. By this mechanism, a radical site can migrate along a polyethylene chain. The hydroperoxy groups are not endlessly stable but will be converted into stable oxygen-containing groups such as carbonyls or carboxyls. In contrast to the initial hydrogen functions, these oxygen functions have increased polarity. Polar liquids can interact with the polar surface groups by long-reaching electrostatic forces. With increased density of polar surface groups, the surface energy grows and polar liquids such as water can more easily wet the material and spread over the surface.[20,21]

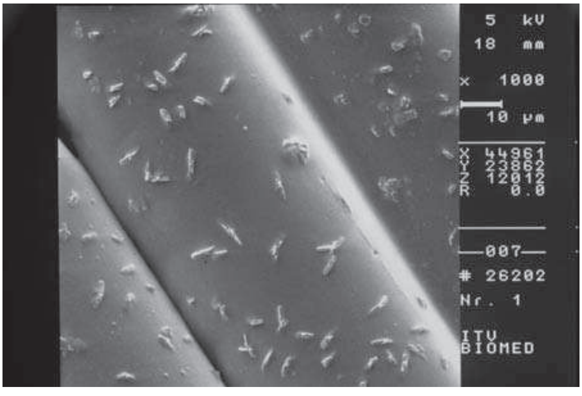
The described reaction mechanisms had been confirmed by X-ray photoelectron spectroscopy (XPS). By XPS, the relative frequency of atoms in the top surface layer and their specific states of chemical bonds can be measured. For example, the ratio of oxygen to carbon can be determined, which can be used to prove the significantly increased oxygen concentration on air-plasma treated polyethylene or polypropylene surfaces.[22]

The duration of the plasma treatment is of importance. In general, the longer the plasma treatment lasts, the more oxygen can be chemically bound to the surface. Although the surface energy might not change any further after a specific treatment time, a prolonged plasma treatment will delay a decay of the effect after stopping the exposure. However, the plasma treatment should be run as short as possible not only for economic reasons; a long plasma treatment can also damage the fibrous substrate.

A plasma source always emits UV radiation. Some UV sources are even based on dielectric barrier discharges. In contrast to the plasma-generated particles, the UV radiation can penetrate deeply into the bulk substrate. A scission of chemical bonds can be the result, which might reduce the tear strength of the fibre.

It has also been observed that oligomers accumulate at the surface of plasma-treated polymers after long exposure. Oligomers are short fragments of polymers with approximately 10–30 repeating units. The oligomers are either generated directly at the surface or migrate from lower layers to the surface, by diffusion. The oligomers are non-reactive and have only weak adhesion to the substrate and therefore spoil the effectiveness of a plasma treatment. Plasma-induced degradation of polymers (Figure 5.4) can often be detected by scanning electron microscopy, showing increased roughness of a former smooth surface. But already a covering of the surface by oligomers can affect adversely the adhesion of coatings.[23–25]

The previously described example of improved coating of plasma pretreated glass fabrics (Section 5.3.1) reveals the importance of improved wettability of the textile substrate by the liquid or paste-like coating in order to improve its adhesion. Any unspecific chemical surface modification that increases the surface energy is likely to raise the adhesion strength of coatings. In the case of glass fabrics, the plasma treatment probably does not chemically modify the glass fiber itself but organic residues on the glass fibre. This is likely because the relatively low electron energies between 1 and 8 eV within dielectric barrier discharges are sufficient to break covalent bonds such as C—H and C—C, but they are not sufficient to break the



5.4 Surface degradation of a plasma-treated polyurethane yarn.

strong Si—O bonds of the glass. The improved adhesion of coatings on DBD-treated glass fabrics can be explained by hydrophilic modification of hydrophobic spin finishes and sizing residues on the glass yarns. The water-based dispersion can penetrate deep into the yarn and the coating can enclose every single fibre. The contact area between textile and coating is raised and the tight fit is better. Delamination forces can be transferred to larger surface areas. Beside the local delamination and detachment of the coating from the fibre, cohesive fracture within the coating or glue is enforced.

This differentiates the plasma-activated bonding and coating of textiles significantly from the pre-treatment of foils or non-porous substrates in general. For those non-porous materials, a chemical modification of the polymeric substrate by reactive functions which support a covalent bond between polymeric substrate and coating is essential. The existence of short-lived reactive sites such as radicals are crucial for improved adhesion to foils, while for porous textiles an improved wettability can be the major reason for better adhesion. Thus, the subsequent processing of plasma-treated textiles can still be possible after storage over days or even weeks because the plasma-induced hydrophilisation is stable over those periods for many substrates. However, the post-processing of plasma-activated textiles should occur as soon as possible to benefit most from the activation and the existence of short-lived reactive functions.

5.3.3 Stability of DBD-treatment effects

It is a common observation that the chemical and physical activity of plasma activated polymeric surfaces diminishes with time. Although the chemical bonds that are generated by the plasma treatment are stable, the effect of a raised surface energy or chemical reactivity is not endlessly durable. This ageing of the surfaces is of specific relevance for polymers with low glass transition temperatures. Materials such as polypropylene or silicones have very high polymer chain mobilities. They age rather fast and the effects of plasma activation are often lost after a day of storage under normal conditions.[26–28] The explanation for this phenomenon is seen in the fact that the high surface energy condition of a plasma-treated polymer is an energetically unfavoured metastable state. A reorientation of polar molecules to each other and a migration of unpolar groups to the surface results in an energetically favoured state, where the polar groups are buried within the bulk and are therefore ineffective. If the polymer has large amorphous fractions at the surface, or the glass transition temperature is low, such reorientations can take place soon after the surface modification. Due to this mobility-based effect, high diffusion rates and storage at elevated temperature will accelerate the ageing process.

XPS analysis of air-plasma treated surfaces over a long time demonstrates the loss of even chemically stable functional plasma-induced groups with time. The oxygen/carbon ratio at the surface slowly decreases without the presence of potential reaction partners and under normal conditions that exclude a chemical reduction of the oxygen containing groups.[22]

The ageing of plasma-induced surface activation effects does strongly depend on the material. It can be diminished by cross-linking the activated surface, which can result from the plasma treatment as well. If the surface becomes cross-linked by breaking and recombining of chemical bonds, the chain mobility is decreased and the stability effect increases.

Very stable plasma activation effects can, on the other hand, be observed with polar or crystalline polymers such as cotton or polyester (PET). In experiments air-DBD-treated cotton warp yarns have remained hydrophilic over at least 3 weeks and activated polyester felts kept their plasma induced hydrophilicity over 2 years of storage.

Beside the influence of the pure fiber polymer, the durability of a plasma treatment depends also on usage conditions and other chemical parameters. Because the plasma modification only affects a very thin, monomolecular top layer, the effect is always modified by friction and abrasion. Polymeric additives also might have influence on the effect and stability of plasma treatments, as well as spin finishings, sizing agents and other functional finishing agents. If they cover the whole fibre, only those finishing agents will be modified by the plasma treatment.

5.4 Deposition of nano-layers by gas polymerisation

Plasma treatments of textiles are not limited to relatively unspecific activations of the textile surface. The gas within the discharge controls the discharge behaviour as well as the formation of reactive species. If reactive gases that are able to polymerise after excitation in the discharge are fed into the plasma zone, thin coatings can be deposited on the substrate from a non-equilibrium plasma by, for example, radical polymerisation.

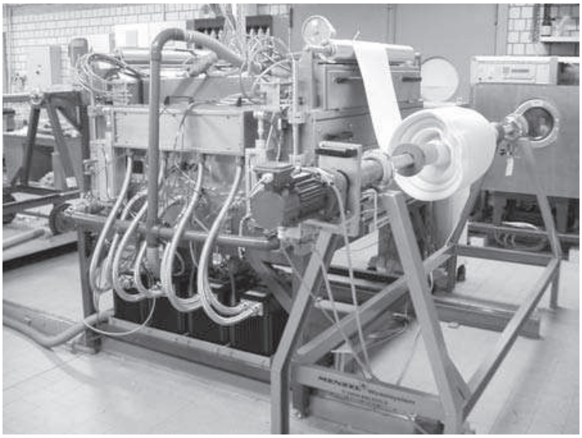
The morphology of the coating and the deposition rate are controlled by the reaction mechanism and reaction rate. Readily polymerising systems form particles within the discharge, which can be deposited on the substrate. However, for textile treatments, these dust-forming plasmas are less relevant because the particles typically lie loosely on the surface.

Of much higher interest are polymerisation processes which predominantly take place at the substrate surface, forming a permanent functional surface coating. For example, highly cross-linked layers with varying surface energies, depending on the chemical composition, can be deposited from non-equivalent plasmas:

- C—H—O-containing layers with compositions $C_{0.6-0.75}$ $O_{0.01-0.05}$ $H_{0.2-0.35}$, formed in hydrocarbon atmospheres generate surfaces with surface energies between 45 and 56 mN/m.[29]
- From organosilicone-containing atmospheres, SiO_2-like coatings with surface energies up to 66 mN/m as well as low energy silicone-like layers with 30 mN/m can be created.[22]
- Coatings with very low surface energies can be generated with gaseous fluorocarbon precursors. PTFE-like surfaces are very hydrophobic because their surface energy lies below 20 mN/m. Responsible for the plasma polymerisation of fluorocarbons and the efficient formation of PTFE-like layers is the bi-radical and reactive fragment CF_2. This polymerisable molecule results from the discharge-initiated fragmentation of fluorocarbons. Together with other fragments such as CF_3 or CF, a highly cross-linked polymeric coating can be deposited via surface reactions on the substrate.[7,22]

For plasma coating processes, the plant design needs to be more complex than the relatively simple constructed surface-activation modules. Compared with the one-step surface activation process, plasma polymerisation is a slow multi-step process. The polymeric chain growth is initiated by fragmentation in the plasma and completed by polymer and network formation at the surface of the substrate. Therefore, to create a functional polymeric surface layer of adequate thickness from gaseous monomers, a sufficient residence time of the precursors and the substrate within the plasma zone is needed in order to form the activated monomers, transport them to the surface, and carry out the surface polymerization. Beside plasma residence time and plasma energy dose, the layer-forming plasma processes also depend on reaction processes occurring without or outside the plasma discharge. Because of this, a pulsed plasma source is of advantage for the plasma polymerising processes.[30]

Open plasma devices as are typically used for continuous surface activation of webs are not suited for plasma polymerisation. In order to define and control the necessary gas composition in the reaction zone accurately, and even to be able to run the plasma process under exclusion of air components (oxygen or nitrogen free), an encapsulation is necessary. In Figure 5.5, a device for plasma coating of textile webs is shown. The prototype has been designed to fulfil both the demands of the academic and industrial developer for efficient process development and the textile industry for industrial use. Salient features are easy loading and unloading, integration into an in-line coating line, treatment widths of 1 m, up-scale possibilities, various modules for monitoring and varying the gas balance, and separate control of all electrodes. A simply designed in- and outlet module for the



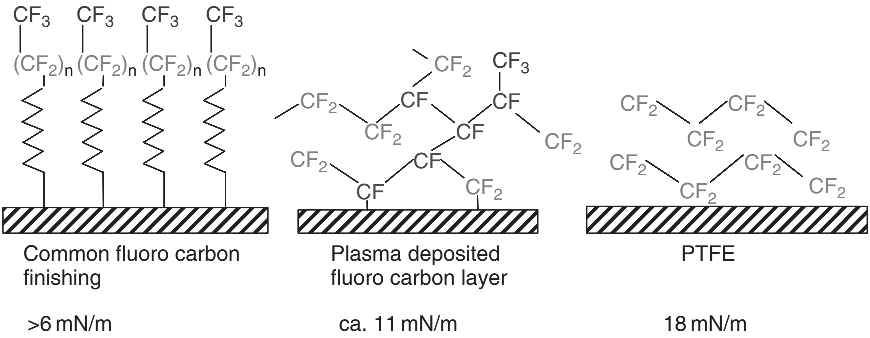
5.5 Enclosed device for continuous plasma coating of up to 1 m wide webs.

textile, acting as a gas lock to remove air fractions from the textile before entering the plasma chamber, even allows a continuous in-line roll-to-roll processing of textiles.

5.4.1 Hydrophobic and oleophobic treatment by DBD

The generation of water- and oil-repellent functional layers on textiles by plasma polymerisation of fluorocarbons at atmospheric pressure under continuous in-line conditions has been a major issue in collaborative research projects at ITV Denkendorf.[31]

The structures of plasma polymerised fluorocarbon coatings are characterized by a relatively high degrees of cross-linking, which can be deduced from CF-group detection by XPS-analysis.[32] The molecular structures and specific chemical functionalities of the used gaseous precursors are only rudimentarily found in the cross-linked deposited layer. The surface energies strongly depend on the density of CF_3-groups at the fluorocarbon surfaces. Schematic structure models of common fluorocarbon textile finishings, PTFE and plasma polymerised fluorocarbons in Figure 5.6 illustrate this. The highest degree of oil repellence can be achieved with perfluorinated side group functionalised resins. With ideally arranged CF_3 groups, the surface energy can be decreased down to 6 mN/m. On the other side, since PTFE contains no CF_3 functions but only CF_2 groups, PTFE has a higher surface energy, approximately 18 mN/m, which is insufficient for oil repellence on textiles. For the formation of plasma-generated oil-repellent fluorocarbons, the choice of precursors and the process parameters have to be



5.6 Schematic structure models of different fluorocarbon surfaces.

optimised so that both an efficient CF_2-based layer formation and a densely CF_3-functionalised surface are realised.

XPS analysis of plasma generated fluorocarbon layers show the need for a precise and continuous control of the atmosphere within the reaction chamber and the plasma zone in order to achieve reproducible and effective polymerisation processes. The plasma polymerisation of fluorocarbons is markedly sensitive towards even small amounts of oxygen in the plasma zone. With oxygen concentrations above 1%, the oxygen in the deposited coating is increased at the expense of a decreased fluorine content, which significantly lowers the oil repellence of the treated textile.[33,34]

With the current state of the art of plasma polymerisation of fluorocarbons at atmospheric pressure, surface energies of 11 mN/m on foils have been achieved. These are significantly lower than the typical 18 mN/m for PTFE. After treating textiles by plasma polymerisation of economical, market-available fluorocarbons at atmospheric pressure under continuous in-line conditions, good oil repellence could be detected.

In two trials (i) a polyester monofilament fabric, treated at a velocity of 0.5 m/min, proved to be oil-repellent Grade 5-6 according to the AATCC 118-1992 standard. (However, the effectiveness of common water-based fluorocarbon resins – oil repellence Grades 7–8 after application – has not been reached so far.) (ii) a fluorocarbon plasma treatment of a hydrophilic fabric of texturized polyester/polyamide yarn (90 g/m^2) reduced the water absorption and water retention properties of the fabric by 60–70%.

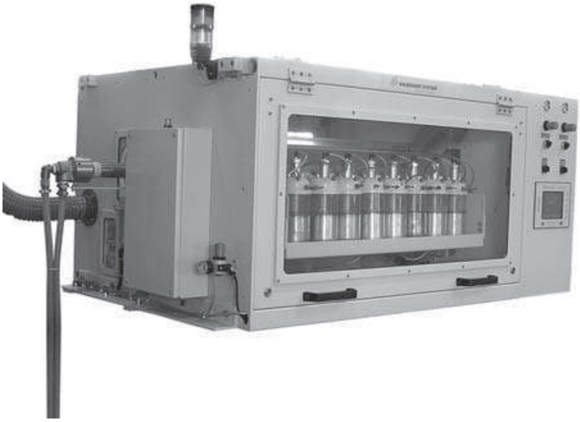
The hydrophobic and oleophobic fluorocarbon plasma-generated coatings are stable. On a plasma-treated polyester felt the oil repellence was found to consistent over the measurement period of 9 months and beyond.

5.5 Combination of DBD treatment and liquor deposition

The use of aerosols within plasma processes is restricted to atmospheric pressure plasmas but widely expands the number and kind of suited chemicals for atmospheric plasma processes. By means of aerosols, chemicals that are liquid at atmospheric pressure, solutions, or even dispersions, can be used in combination with a plasma process for surface functionalisation.

5.5.1 DBD systems in combination with aerosols

Systems for DBD treatment in combination with aerosols are commercially available, such as the *AS Coating Star* module of the company Ahlbrandt System (Figure 5.7). This system contains one or more aerosol generators and a specific electrode housing with an aerosol inlet in addition to the common ceramic-coated roller and bar electrodes. The aerosol-generating nebulisers are positioned directly in front of the electrode housing and generate, by means of pressurised gases, e.g. air or inert gases, floating levitated aerosols from usually aqueous solutions, with an average droplet diameter below 1 µm. 1 ml aerosol solution equals $2 * 10^{12}$ (2 trillion) droplets of 1 µm diameter. These droplets are directed, with the nebuliser gases and additional transport gases, through a system of slot dies into the plasma zone. The amount of aerosol is controlled by the gas flow of the nebuliser gases while the volume flow of the transport gases regulates the velocity of the gas/aerosol phase entering the discharge region. The gas–aerosol ratio



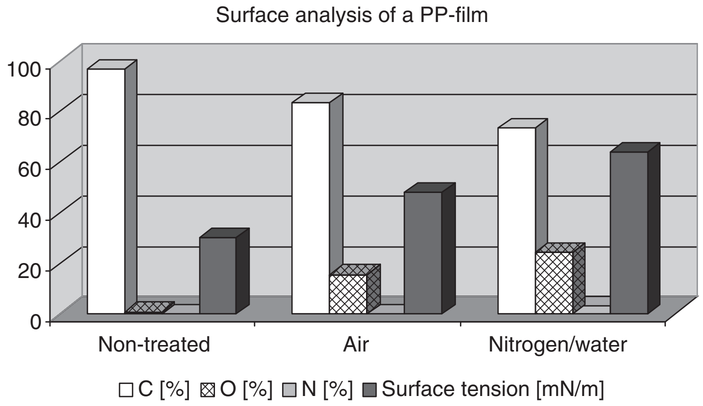
5.7 Corona system with eight nebulisers for aerosol application.

can be adjusted at the same time. Depending on the temperature of the heatable nebulisers, the maximum output of aerosols is 200 ml/h per nebuliser. The regulation of the aerosol throughput is first of all controlled by the number of nebulisers within the system, beside the gas flow regulation. A typical number of nebulisers is 1–10 per 1 m working width. The viscosity of the fluids should be below 100 mPa s. If possible, only solutions should be used. The use of dispersions has to be checked in every case and only nm-scaled dispersed particles can be considered. Because of these boundary conditions, the concentration of functional additives is between 1 and 10% in most cases. This determines the amount of applicable substances. Depending on the web velocity, the maximum substance application lies between 1 and 100 mg/m^2.

It is advantageous to make the slot dies exchangeable and freely positionable. The aerosols can then be applied either outside the discharge in front of or behind the electrodes, or directly into the discharge between the electrodes. It depends on the aimed functions whether it is better to choose a nozzle position that applies the aerosols to the substrate before it enters the discharge or after leaving the discharge, or to a position that injects the aerosol into the most active plasma zone. Feeding of the aerosols behind the electrodes avoids fragmentation and destruction of functional substances, as well as undesired layer deposition on the electrodes. Such a configuration is suited for anti-static or anti-microbial finishings. The application of simple, commercially available, non-toxic, water soluble polymers results in anti-bacterial properties with partially very high durability.

This method of gas/aerosol application is, in general, best suited for substances that are effective also in low concentration. The necessary effective dosage of the functional additives limits the maximum web velocity. Depending on the textile application, web speeds are below 10 m/min.

An injection of the aerosol into the most active discharge zone allows plasma-activated reactions. The discharge characteristics are strongly influenced by the concentration and kind of the induced substances. In this configuration, it is possible that the high-voltage electrodes become unintentionally coated. This contamination might degrade the plasma efficiency. Such problems are avoided by a process which uses water aerosols in a nitrogen atmosphere in order to achieve exceptionally high surface energies. The electrode temperatures of above 150°C let the water droplets quickly evaporate. In the resulting homogeneous plasma discharge, the molar fraction of water in the plasma atmosphere can be very high. Such a plasma achieves a much higher surface energy on polyolefines or polyester compared with simple barrier discharges in air with the same corona energy. Besides a better wettability, the treated surface also demonstrates better adhesion of subsequent coatings, which can be explained by a higher density of functional groups at the substrate surface (Figure 5.8).



5.8 Comparison of surface properties (atom content on surface measured by XPS and surface energy measured by test inks) of an untreated polypropylene foil, a PP-foil treated in standard air-DBD and a PP-foil treated in nitrogen-DBD in combination with a water aerosol.

The very high fraction of oxygen containing groups on the water/nitrogen–aerosol–plasma-treated polypropylene surface has to be explained by the water fraction in the plasma atmosphere being the only significant oxygen source, because the oxygen concentration within the nitrogen/water plasma is below 1%. While barrier discharges in air primarily result in a generation of peroxy functions on the substrate by activating O_2 molecules, a discharge in nitrogen/water atmospheres creates mainly OH-functions. Without any other additives, plasma-activated pure aqueous aerosols avoid undesired coating of the electrodes, making this process configuration free of maintenance.

5.5.2 Current developments for improved DBD use and effectiveness

The operational costs of atmospheric pressure plasma processes are strongly influenced by the kind and consumption of the used gases. The most economic option is a discharge in air or a combination of air discharge with liquid aerosols. However, as discussed above, this process is limited to small quantities of applicable substances. Therefore, other application systems which can apply larger substance quantities, as are for example necessary for hydrophobic treatment at higher web velocity, are currently under development.

The use of nitrogen is the most economic option for oxygen-free or inert gas based atmospheric-pressure plasma processes. Depending on working width and web velocity, a typical nitrogen consumption lies between 10 and 100 m^3/h. A significant cost reduction can be achieved by re-feeding the used nitrogen. Such recirculation devices are already developed and have to be tested in continuous operation.

If textiles are to be treated continuously by a continuous oxygen-free or inert gas based plasma treatment, the gas locks at the plasma chamber entrance and exit need specific attention. The undesired entrainment of oxygen or other air fractions by the substrate into the chamber and the discharge gap rises proportionally to the volume and the web velocity of the textile. While for treatments of foils and flat substrates the oxygen entrainment is independent of the substrate, for textile treatments the specific textile properties play an important role. A test series is necessary for each substrate to adjust each parameter in order to stay within the tolerances of acceptable remaining oxygen concentrations.

An alternative to the very fine aerosol producing nebulisers are spraying devices that use fast rotating discs. The generated droplets are bigger than 1 μm and larger quantities of liquid substances can be applied. An enclosed 1 m pilot plant at ITV Denkendorf is equipped with such a spraying device. Due to its principal and required space, this spraying device cannot be placed very close to the discharge region. However, water-based textile finishing agents can be applied immediately after the activation of the textile in the dielectric barrier discharge.

It will need further R&D efforts to tap the full potential of a combination of aerosols from nebulisers or spraying modules with the dielectric barrier discharge for surface functionalisation of textiles. Examples for current and future developments are:

- physical surface modification, e.g. to generate electret properties
- chemical functionalisation
- minimal application and energy efficient finishing processes
- chemical and topographical nano-structuring.

5.6 Future trends

Plasma systems that allow the surface treatment of substrates independent from substrate porosity, area size and topography will be of specific interest for the processing of textiles. Systems that are independent of the position of a counter electrode seem capable of this. In conventional systems, for example, the maximum substrate thickness is limited by a maximum discharge gap between electrode and counter electrode. Systems with so-called indirect or remote plasma sources are able to penetrate into thick textile substrates and homogeneously modify three-dimensional structures. A special challenge is the design of an adequate plasma system for the typical wide working width of textiles.

5.6.1 Developments in discharge technologies

Low-pressure plasma treatments for surface functionalisation and coating have a broad field of application in the processing of semiconductors, optical and medical devices and machinery manufacturing.

Non-thermal atmospheric-pressure plasma technologies have led a shadowy existence beside the corona treatment of polymeric surfaces. However, in recent years it has been shown that a number of non-thermal processes, even CVD processes, which were limited to low pressure plasmas, could be successfully transferred to the atmospheric pressure range. Starting points were the plasma technical developments of individual plasma sources such as Dielectric Barrier Discharge, arc-jet, microwave and hybrid plasma sources. The new plasma sources are generally usable for surface modification, substrate pre-treatment, surface cleaning, etching and plasma chemical coating.

Compared to plasma spraying and other thermal plasma treatment techniques, the advantage of non-thermal atmospheric-pressure plasma techniques is the possibility of coating large surfaces of heat-sensitive substrates such as textiles with nano-scale functional layers.

The treatment width of such plasma systems varies widely, starting at a few millimetres (coplanar discharges, jets). These plasma sources can be scaled up to larger treatment width by arranging arrays of single sources. Surface patterning can be realised by structuring dielectrics via print-like methods generating hollow discharges.

Two systems can be differentiated in the field of atmospheric-pressure plasma deposition processes:

(i) Precursors, either gaseous or as aerosols, are applied directly into the discharge gap where the plasma is generated. Plasma chemical deposition of fluorocarbons and silicon oxide layers have been realised on pilot plant scale.
(ii) By means of remote processes, the plasma generation and the activation zone of the precursors are separated. Deposition rates of 100 nm/s are possible.[35]

5.6.2 Developments in computer simulation

The on-going expansion of fundamental knowledge about the generation and effect of plasmas, in combination with further evolving software and hardware for numerical simulations, are the bases of simulations of the chemical/physical processes of plasma treatments. Numerical simulations can support the optimised design of plasma devices with regard to gas flow, electrical modules and effect.

5.7 References

1. Inagaki, N., *Plasma Surface Modification and Plasma Polymerization*, Technomic Publishing, Lancaster (1996).
2. Bahners, T., Best, W., Ehrler, P., Kiray, Y., Lunk, A., Weber, N., 'Barriereentladung bei Atmosphärendruck als In-line Veredlungswerkzeug zur Hydrophilierung über Hydro- bis Oleophobierung' *Proc. 26th Aachen Text. Conf., Nov. 1999, pp 7–15*, Aachener Textiltagung (1999).
3. Stegmaier, T., Bahners, T., 'Plasmabehandlung unter Atmosphärendruck an laufenden Textilbahnen', *Avantex-Symposium*, Frankfurt, 27–29, 11, 2000, Technische Textilien, April 2001.
4. d'Agostino, R., Favia, P., Oehr, C., Wertheimer, M.R., 'Low-temperature plasma processing of materials: past, present, and future', *Plasma Processes and Polymers*, **2** (1), 2005. Pages 7–15.
5. Janzen, G., *Plasmatechnik: Grundlagen, Anwendungen, Diagnostik*, Hüthig Verlag, Heidelberg, 1992.
6. Akishev, Yu., Grushin, M., Kochetov, I., Karal'nik, V., Napartovich, A., Trushkin, N., 'Negative corona, glow and spark discharges in ambient air and transitions between them'; *Plasma Sources Sci. Technol.* **14** (2005) S18–S25.
7. United States Patent 6,827,781, Hahne *et al.*, 'Device for humidifying a material web'.
8. Sumorek, A., Pietrzyk, W., 'The influence of electric field on the energy consumption of convective drying processes'. *Agricultural Engineering International: the CIGR Journal of Scientific Research and Development*. Manuscript FP 00 017. Vol. III.
9. Stegmaier, T., Abele, H., Planck, H., 'Energieeinsparung und Reduzierung der Trocknerlänge bei IR- und Konvektionstrocknern', *Melliand Textilberichte*, 5/2005.
10. Knopf, F., *Deutscher Drucker*, **27** (2003) 26–28.
11. Vinogradov, G.K., *Proceedings ISPC Praha*, **12** (2000) 1867–1872.
12. Kogelschatz, U., 'Dielectric-barrier discharges: their history, discharge physics, and industrial applications', *Plasma Chemistry and Plasma Processing*, **23** (1), (2003), 1–46.
13. Eliasson, B., Kogelschatz, U., 'Modeling and applications of silent discharge plasmas', *Plasma Science, IEEE Transactions*, **19** (2), Apr 1991 Pages 309–323.
14. Eliasson, B., Kogelschatz, U., 'Nonequilibrium volume plasma chemical processing', *Plasma Science, IEEE Transactions*, **19** (6), Dec. 1991 Pages 1063–1077.
15. Menges, G., Michaeli, W., Ludwig, R., Scholl, K., 'Koronabehandlung von Polypropylenfolien', *Kunststoffe*, **80** (1990) 11.
16. Herbert, P.A.F., Bourdin, E., 'New generation atmospheric pressure plasma technology for industrial on-line processing', *Journal of Coated Fabrics*, **28** (1999).
17. Gerhard, A., WO03099530, 'Device for perforating a web-type material'.

18. Teschke, M., Korzec, D., Finantu-Dinu, E.G., Engemann, J., ‘Plasma cleaning of “endless” substrates by use of a tandem dielectric barrier discharge’, *Surface and Coatings Technology*, **200**, (2005) 690–694.
19. Gerstenberg, W., ‘Korona-Vorbehandlung zur Erzielung von Benetzung und Haftung’, *Coating*, **7** (1990).
20. Tahara M., Cuong N.K., Nakashima Y., ‘Improvement in adhesion of polyethylene by glow-discharge plasma’, *Surface and Coatings Technology*, **174**: 826–830 Sep–Oct 2003.
21. Holländer A., Kröpke, S., ‘Radikale bei der Plasmabehandlung von Polymeren’, *Workshop Oberflächentechnologie mit Plasma- und Ionenstrahlprozessen*, March 2003, Mühlleithen.
22. Arpagaus, C., Rossi, A., von Rohr, Ph.R., ‘Short-time plasma surface modification of HDPE powder in a Plasma Downer Reactor – Process, wettability improvement and ageing effects’, *Applied Surface Science* **252** (2005) 1581–1595.
23. Friedrich J.F., Unger W.E.S., Lippitz A., *et al.*, ‘Chemical reactions at polymer surfaces interacting with a gas plasma or with metal atoms – their relevance to adhesion, *Surface and Coatings Technology* **119**: 772–782 Sep 1999.
24. Friedrich J., Loeschcke I., Frommelt H., *et al.*, ‘Aging and degradation of poly(ethylene-terephthalate) in an oxygen plasma’, *Polymer Degradation and Stability* **31** (1), 97–114 1991.
25. Eggert L., Friedrich J., Wittrich H., *et al.*, ‘Plasma-etching of thin-layers of organic polymers. 3 – Phenomenological mechanism of etching’, *Acta Polymerica*, **41** (11), 569–574 Nov 1990.
26. Kim, J., Chaudhury, M.K., Owen, M.J., Orbeck, T., ‘The mechanisms of hydrophobic recovery of polydimethylsiloxane elastomers exposed to partial electrical discharges’, *Journal of Colloid and Interface Science*, **244**, 200–207 (2001).
27. Novák, I., Florián, E., ‘Influence of ageing on adhesive properties of polypropylene modified by discharge plasma’, *Polymer International*, **50** (1), January 2001, pp. 49–52(4).
28. Dorai, R., Kushner, M.J., ‘A model for plasma modification of polypropylene using atmospheric pressure discharges’, *J. Phys. D: Appl. Phys.*, **36** (2003) 666–685.
29. Klages, C.-P., Eichler, M., Penache, C., Thomas, M., *Plasmagestützte Oberflächentechnik ohne Vakuum,* Geesthachter Innovations und Technologie Centrum (GITZ) Geesthacht, 2005.
30. Vinogradov, I.P., Shakhatre, M., Lunk, A., ‘Diagnostics of a dielectric barrier discharge afterglow running in Ar/C_xF_y mixtures’, *Verhandl. DPG (VI)*, **40**, page P14.3, 2005.
31. Stegmaier, T., Arnim, V. v., Dinkelmann, A., Planck, H., ‘Behandlung von laufenden Textilbahnen im Atmosphärendruckplasma’, *Melliand Textilberichte*, **6** (2004), 476–481.
32. von Arnim, V., Stegmaier, T., Praschak, D., Bahners, T., Lunk, A., *et al.*, ‘Continuous plasma treatment of textiles under atmospheric pressure’, *Proceedings of the 29th Aachen Textile Conference*, DWI an der RWTH Aachen Univ., 2002.
33. Vinogradov, I.P., Lunk, A., ‘structure and chemical composition of polymer films deposited in a dielectric barrier discharge (DBD) in Ar/fluorocarbon mixtures’, *Surface and Coatings Technology*, **200**, (2005) 660–663.

34. Vinogradov, I.P., Lunk, A., 'Dependence of surface tension and deposition rate of fluorocarbon polymer films on plasma parameters in a dielectric barrier discharge (DBD)', *Surface & Coatings Technology*, **200**, (2005) 695–699.
35. Dani, I., 'Atmosphärendruck – PECVD zur Grossflächenbeschichtung', *Workshop Oberflächentechnologie mit Plasma- und Ionenstrahlprozessen*, March 2004, Mühlleithen.

6

Nano-scale treatment of textiles using plasma technology

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6.1 Introduction

This chapter highlights the aspect of nano-scaled treatments of textiles in different ways. Briefly, plasma technology can be used for ablation and deposition processes. While ablation enables a complete cleaning of textiles from manufacturing residuals, deposition can be controlled in the nanometre range to achieve new functionalities. The textile properties remain unaffected with both treatments and they are dry and eco-friendly processes. Section 6.2 thus shows some advantages of plasma technology for the textile industry besides looking at the gain from nano-size (dimension of 10^{-9} m). Section 6.3 deals with materials and methods with respect to the pressure range (atmospheric or low pressure plasma) and plasma reactors. Section 6.4 examines the effectiveness of plasma cleaning, focusing on fabrics, fibres, and the scale-up of the presented methods. Sections 6.5 and 6.6 are similarly organised, considering plasma metallisation and plasma polymerisation, respectively. They investigate the special requirements for fabrics and fibers to achieve nano-scaled coatings, as well as the transfer to industrial-size processes (scale-up). 'Plasma co-polymerisation' (Section 6.7) describes a combination of sputtering and plasma polymerisation to obtain nanoparticles within a polymeric matrix. The benefit of this new approach is outlined. 'Future trends' (10.8) and 'Further information' (10.9) complete the chapter.

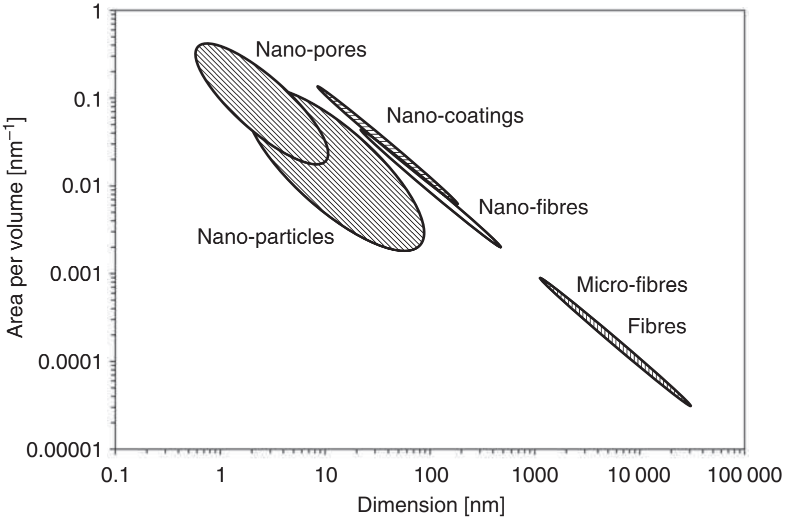
6.2 Plasma technology for the textile industry

The challenges the textile industries of Europe and North America are facing today are enormous. Therefore, the need for a reorientation is strong. In order to survive, the transition to a knowledge-based economy focusing on high-value added products is needed. Plasma technology offers an attractive way to add new functionalities to textiles, such as water and stain repellence, hydrophilicity, conductivity, biocompatibility as well as new or improved mechanical, optical and tribological properties.

The plasma state consists of an equal part of negatively and positively charged particles (quasi-neutrality), excited states, radicals, metastables and vacuum ultraviolet (VUV) radiation. Surface treatments of materials can be performed by non-equilibrium plasmas, which are excited by electric fields. Since the energy coupling is conducted by electrons, which achieve a mean temperature of several electron volts (corresponding up to 100 000 K), the main part of the plasma-activated gas remains close to room temperature. The electrons, however, gain just the right energies to excite, dissociate and ionise atoms and molecules. The degree of ionisation typically lies between 10^{-4} and 10^{-6}. The reactive plasma particles and radiation yield a nano-scaled interaction with material surfaces by chain scission and cross-linking reactions, radical formation, etching or deposition. The bulk properties of materials can thus be maintained. Textiles and fibres differ from other materials mainly by their complex structure showing openings at different length scale (micro- to nanometre range) such as filament or interfibre distances, resulting in higher surface areas.

An important characteristic of the nano-scale ($1\,\text{nm} = 10^{-9}\,\text{m}$ or a millionth of a millimetre) is also the increasing surface area with respect to the bulk material. Hence, surface sensitive processes strongly benefit from nano-technology. This effect is already used for micro-fibres, since their fineness improves, for example, wicking and softness. Nano-fibres showing even higher areas per volume are used, for example, for air filtration. The deposition of nano-scaled coatings on textiles, starting at several nanometres in thickness to obtain a complete coverage of the textile surface, can provide a high surface functionality, e.g. for adhesion or wettability improvement, while using a low amount of material. Nano-particles embedded in a surface layer or a coating are used for drug release and photo catalytically active or anti-microbial interfaces. Their area per volume ratio also depends on the density of the nano-particles within a matrix and their size distribution. Nano-porous coatings containing a high amount of accessible functional groups show the highest area per volume ratio, which depends on porosity, for pore sizes around 1 nm (Figure 6.1). These coatings are of high interest for their dyeability and as anti-fogging or non-fouling surfaces.

Using plasma technology to modify textile surfaces, etching and deposition reactions can be used to obtain nano-particle or nano-porous structures. Moreover, it is a dry and eco-friendly technique, avoiding waste production as found in wet-chemical processes. However, for the transfer into industry, both the feasibility of scale-up and economic aspects have to be regarded.



6.1 Surface area per volume depending on the size of different structures. The area per volume is proportional to the inverse length scale (diameter of fibres, thickness of coatings, size of particles and pores). The density of the nano-particles is taken as 5 to 50% and the porosity of the nano-porous coatings as 10 to 40%.

6.3 Materials and methods

In principle, all types of textile materials may be treated within a plasma (Kang, 2004a, b). Considering the nano-scaled treatment of textiles using plasma technology, however, the special geometry, manufacturing residuals (sizes) and additives, as well as the water content, have to be taken into account. The structure of the considered textile will show several dimensions, including the filament distance and the interfibre (yarn) distance, as well as contacting areas or protruding fibre ends. Thus, different treatment conditions due to different incident angles of reactive particles and shadowing effects can be expected for different fibre surface areas, complicating a homogeneous treatment. The mean free path (pressure), the lifetime (reaction probability) and the width of the plasma sheath surrounding the substrates determine the type of active particles that might reach the substrate surfaces and contribute to the treatment. Manufacturing residuals might cover the entire fibre surfaces, requiring a cleaning step prior to the plasma functionalisation of textiles. Moreover, desorption from textiles as well as etching or sputtering products might substantially change the plasma gas composition. Outgassing of textiles also yield a more intense VUV radiation by H_2, H_2O, and CH gas desorption (Wertheimer, 1999).

In the following, we mainly consider textile fabrics and fibres as examples for two different textile geometries. However, knitwear, non-wovens, paper or membranes can be treated analogically to fabrics.

6.3.1 Pressure range

The pressure range selected for textile treatments using plasma technology strongly influences the achievable functionalisation effects, but determines also the required plasma equipment (Hegemann, 2006a). For the textile industry, mainly plasma systems running under atmospheric pressure seem to be of interest, to enable a continuous process. Corona discharge treatment in air, used industrially since the 1950s, still represents a major process for surface activation of polymers, textiles, and other flexible substrates of simple geometry. Corona discharges, operated at high voltage in the 10–20 kHz frequency range, however, are not homogeneous, for they consists of filamentary microdischarges yielding hot spots and damaging textile surfaces. Alternative methods, such as atmospheric pressure Dielectric Barrier Discharges (DBD), on the other hand, lose some of their advantages such as a high process velocity, and encapsulation is required to obtain the more or less defined gas composition required for more advanced plasma treatments. Furthermore, the textile structure hinders the penetration of reactive particles due to low mean free path lengths. Contrary to atmospheric plasmas, low pressure discharges contain energetic particles, long-living radicals, and vacuum ultraviolet (VUV) radiation due to longer mean free paths. Especially, long-living oxygen and hydroxyl radicals formed in low pressure plasmas are able to penetrate into open structures in the micrometre or sub-micrometre range that are found in textiles and membranes (Oehr, 2005; Kull, 2005).

Mainly by the variation of the pressure, the plasma process can be optimised for different treatments and textile structures. Moderate pressure plasmas (100 to 1000 Pa) were found to give optimum cleaning and activation conditions with non-polymerisable gases since a high number of active particles contribute to chemical etching (Poll, 2001; Keller, 2005). Plasma polymerisation can best be controlled using low pressure plasmas (1 to 100 Pa), due to well-defined plasma zones (Hegemann, 2006a). In this pressure range, the mean free path lengths are high enough to allow the penetration of the textile structure by energetic particles and long-living radicals. Good conditions for plasma polymerisation are thus enabled on textile fibres up to several fibre layers in depth, such that external media interact with the treated fibres. Sputtering processes, finally, are carried out in the pressure range between 0.5 and 5 Pa to avoid in-flight scattering collisions of the background gas and the sputtered atoms (Rossnagel, 2003). Therefore, at the authors' institute (Empa), mainly low-pressure plasmas are considered to obtain nano-scaled treatments on textiles.

6.3.2 Plasma reactors

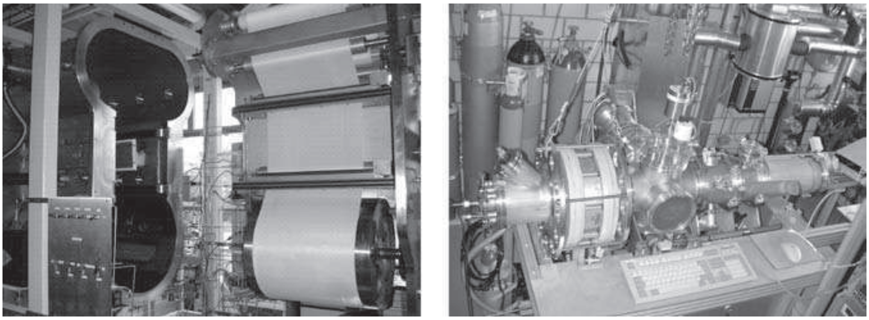
To build a reactor for plasma polymerisation on textiles, a vacuum chamber is required to enable low-pressure plasma processes. In a vacuum it is easier – at least when different types of textile fabrics, non-wovens, membranes, and papers are to be treated – to have the winding inside the chamber, enabling a semi-continuous treatment. Obviously, this kind of process cannot be integrated directly into a production line.

Large reactors for low-pressure plasma treatments on textiles are available. Plasma excitation in the kilohertz range (typically 40 kHz) is mainly used for industrial purposes due to lower costs. Radiofrequency (RF) or microwave (MW) sources are also applicable, if required by the process. The reactors are typically designed for textile widths up to 120 cm: larger widths (up to 4 m) are possible. The reactors are loaded with textile materials, closed, evacuated and run in a semi-continuous process from reel-to-reel. The textiles are led through the plasma regions adapted to the required process, which comprises usually a cleaning and a plasma deposition step.

To avoid some limits of plasma polymerisation on fabrics or other webs (huge reactor, semi-continuous process, fibres contacting other fibres), the direct treatment of fibres is also of importance. One advantage of fibre processing is the possibility to perform unwinding (before plasma treatment) and winding (after plasma treatment) in air by leading the fibres through suitable openings into the low pressure region using a differentially pumped sealing system. A modular set-up by the combination of separated plasma chambers enables different process steps such as plasma pre-treatment (cleaning), deposition, and post-treatment. Flexible textile fibres, yarns, etc. can be run several times through the plasma zones, enhancing the plasma length and thus the process velocity. Furthermore, different treatment times that might be required for different process steps such as cleaning, deposition, and post-treatment can thus be adapted for a one-step processing. In-line production is achievable by process velocities as high as several hundred metres per minute. Therefore, both a (semi-continuous) web coater and a (continuous) fibre coater are present at Empa (Figure 6.2), which serve as pilot-plant reactors to demonstrate industrial scale-up.

The large web coater admits reel-to-reel processing of webs up to a width of 65 cm and a velocity of 100 m/min (corresponding to a treatment time of a few seconds). Three separated treatment zones allow pre-treatment, coating, and post-treatment in one process step. A large drum (62 cm in diameter) in the lower chamber provides a deposition area of around 2 m in length. Depositions can be performed via plasma polymerisation and/or magnetron sputtering.

The unique fibre coater is equipped with an inverse cylindrical magnetron enabling the uniform coating of fibres or wires (Amberg, 2004). Additionally,



6.2 Empa's plasma reactors for web coating (left) and fibre coating (right).

plasma treatment and plasma polymerisation processes can be performed. The fibres are wound and unwound in air and are transported through a sealing system into the vacuum chamber. Velocities up to 100 m/min can be reached with fibre diameters ranging from micrometres to millimetres. Automatically controlled pumping systems using rotary, roots and turbomolecular pumps enable a fast evacuation of the reactor chambers down to a pressure of 10^{-3} Pa.

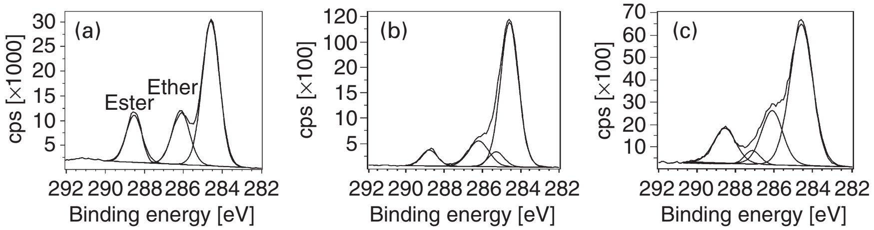
Additionally, batch reactors with different geometries and excitation sources (RF, MW and magnetron sputtering) are used for the optimisation of plasma processes.

6.4 Plasma cleaning

During textile manufacturing, sizing agents, mineral oils or acrylate-based spin finishes are applied, which form a film around the yarn or individual fibers to reduce friction and electrostatic charging. Due to the interaction of reactive plasma species, textile surfaces can be etched physically and chemically. Ion bombardment, radical density and VUV (vacuum ultraviolet) radiation determine the etching rate depending on reactor geometry, plasma excitation, gas type, flow, power, pressure and textile material (Liston, 1993). Typical etch rates of organic materials are a few nanometres per second. Therefore, a plasma treatment can be used for the cleaning of manufacturing residuals on textiles. Plasma cleaning is a prerequisite to obtaining good adhesion, e.g. to a subsequent plasma coating, and can be performed in a one-step process.

6.4.1 Fabrics

Analysis of an industrially washed PET fabric by XPS revealed an enhanced hydrocarbon (C—C, C—H) peak at 284.6 eV compared with a PET



6.3 XPS spectra of (a) PET reference spectrum, (b) PET textile fabric as received (industrially washed), and (c) plasma-cleaned PET textile fabric.

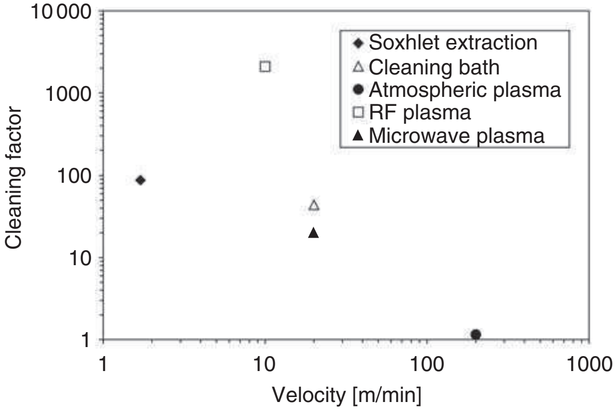
reference spectrum (Figure 6.3). Using Soxhlet extraction, the weight of the residuals can be determined and the corresponding thickness can be calculated. For the as-received textile fabric (industrially washed), a residual layer of 3–4 nm was found, which might be inhomogeneously distributed. This result agrees well with the XPS obtained depth of ~5 nm.

A short plasma treatment using a gas mixture of argon and oxygen (RF plasma, 10 m/min, 0.2 W/cm^2, 20 Pa) totally removes the residual spin finish and leads to an additional activation of the polymer, indicated by new functional groups around 287.2 eV as shown in Figure 6.3 (Hossain, 2006a). While argon causes mainly physical degradation by chain scissions, whereby also redeposition occurs, atomic oxygen produced in the discharge (by energy transfer and VUV light activation through the inert gas) results in chemical etching and the formation of volatile compounds such as CO_2 and H_2O. Hence, a complete cleaning can be obtained by a plasma treatment. However, the plasma cleaning should be adapted to the textile structure of the treated fabric (Hossain, 2006b).

Moreover, a plasma treatment with non-polymer forming gases might be used prior to the grafting of monomers onto fabrics or after the soaking of fabrics within a monomer solution to induce cross-linking (Castelvetro, 2006). Conventional wet-chemical treatments such as pad dyeing with fluorocarbons can also be improved after plasma cleaning and activation to achieve excellent stain repellencies (Hegemann, 2005c).

6.4.2 Fibres

On commercially available, continuous multifilament yarn made of polyester, 4.4 wt% of oily substances were found, which corresponds to an about 180 nm thick contaminant layer (Keller, 2005). A comparison of different cleaning methods on these polyester fibres proved RF plasma cleaning (Ar/O_2 or He/O_2, 10 m/min, ~0.2 W/cm^2, 100 to 700 Pa) to be ideal (Figure 6.4). The velocity can be enhanced by leading the fibres several times through the plasma zone. Moreover, the lowest amount of waste resulted



6.4 Effectiveness and efficiency of different cleaning methods in terms of cleaning factor vs. velocity. The cleaning factor is defined as the ratio of initial to residual contaminants on the PET yarn. A factor exceeding 1000 can be considered as complete removal of the mineral oils.

from the plasma cleaning, demonstrating its potential as an eco-friendly technology.

6.4.3 Scale-up

Plasma cleaning is controlled by energetic particles (physics) and radicals (chemistry). The transfer of plasma activation and etching processes with non-polymerisable gases between various reactors was found to depend on the energy flux to the substrate, which is mainly determined by the sheath voltage, the pressure (by collisions within the plasma sheath) and the plasma power density (power per area) controlling the ionisation degree (Kersten, 2001). Thus, the scale-up of plasma cleaning can easily be achieved by maintaining gas composition and pressure and adjusting the power input regarding the area of the treatment (W/cm^2).

6.5 Plasma metallisation

For the metallisation of textiles, sputter-based processes can be effectively used. Sputtering can be characterised as a non-equilibrium process at the energy range of interest for film deposition (Rossnagel, 2003). Sputtering is initiated by the impact of energetic particles (in the order of 100 eV) on a target material, e.g. a metal. The incident particle causes a multiatom kinetic collision process, whereby atoms near the surface may be dislodged with enough energy to overcome the surface binding energy and be emitted from the target. These atoms are known as sputtered atoms, and when they deposit on some other surface, the process is called sputter deposition. Inert gases such as argon are generally used for the sputtering of metals, whereas an addition of reactive gases (O_2, N_2 etc.) yield reactive sputtering and, e.g. metal oxides or nitrides. Moreover, alloys, ceramics, and polymers can be used as target materials. The energy of the incident particles can be enhanced by electrical and magnetic fields, while avoiding collisions. Therefore, we are mainly using magnetron sputtering with argon at a pressure of 1 Pa to obtain metallisations on textiles and fibres.

6.5.1 Fabrics

Fabrics made of mono- or multifilamentary fibres or yarn show uncovered and covered areas at superposed fibres/filaments. Since sputtering is mainly a directed deposition due to high sticking coefficients of the atom/cluster flux from the target to the substrate, an inhomogeneous film growth on structured surfaces such as fabrics can be expected. To investigate this effect, we deposited copper coatings on tightly woven PET fabrics using DC magnetron sputtering. The substrates were fixed on the rotating drum of our web coater. Treatment times of 15, 30 and 60 min were used at an argon pressure of 1.5 Pa to obtain around 100, 200 and 400 nm thick Cu films, respectively (measured on Si wafers). The surface resistivity on the fabrics was measured according to EN1149-1. The short deposition time of 15 min results in a high resistivity of $10^{13}\,\Omega$, whereas $6 * 10^{10}\,\Omega$ was obtained for 30 min and $10^{10}\,\Omega$ for 60 min of sputtering time. Note that the surface resistivity – though the current is restricted to a thin surface layer – is still dependent on film thickness for nano-scaled coatings on textiles. Hence, the lowest film thickness or disconnected areas along the coated fibres of the fabric, which might be found at superposed fibres (thus also depending on the textile structure), determine the conductivity of a metallised fabric. For an anti-static treatment of fabrics, a surface resistivity below $5 * 10^{10}\,\Omega$ is needed. Depositions of more than 200 nm are thus required to obtain anti-static fabrics by magnetron sputtering due to the inhomogeneous coating. However, thicker coatings show some crack formation detected by scanning electron microscopy. The direct metallisation on fibres is thus of high interest for the deposition of more homogeneous, nano-scaled coatings to achieve a good conductivity by maintaining the textile properties.

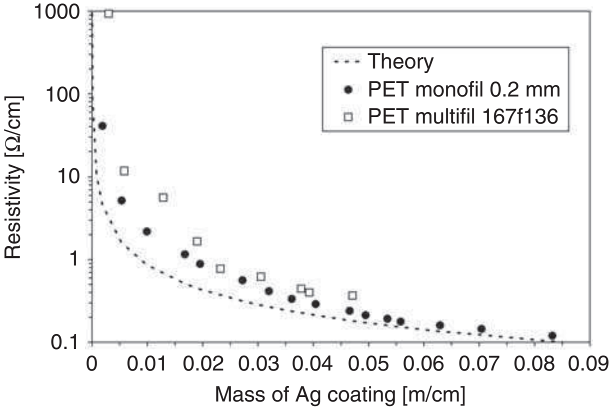
6.5.2 Fibres

Magnetron sputtering of metals on fibres, which can be performed using our fibre coater, provide conductive/anti-static and in the case of silver also anti-bacterial surfaces (Amberg, 2004). After a cleaning step as described in Section 6.4.2, the fibres are metallised in a continuous process by moving them several times through the plasma zone created inside the cylindrical magnetron. Thus, a homogeneous, all-side coating can be achieved. When the fibres are moved back to air, the electrical resistivity is measured online. By variation of the plasma conditions (power: 200 to 4200 W; pressure: 1 to 5 Pa) and the process velocity (0.3 to 80 m/min), the amount of the sputter-deposited metal, i.e. the deposited mass or the coating thickness, can be controlled. If a homogeneous coating without defects is assumed, the resistivity per length of the fibre (in Ω/cm) can be calculated from the deposited mass of the metal per length of the fibre *m*/*l* (in g/cm) by

$$\frac{R}{l} = \rho_{el}\rho\left(\frac{m}{l}\right)^{-1} \qquad [6.1]$$

with the specific electrical resistivity ρ_{el} (in Ω/cm) of the considered metal and its density ρ (in g/cm^3). These theoretical values were compared with real coatings on PET monofilament fibres (∅ 0.2 mm) and PET yarn (167 f144) for different amounts of sputter-deposited silver (Figure 6.5). Note that the deposited mass was used as parameter, since it can be measured more precisely compared to, e.g. the coating thickness. The obtained resistivity was averaged over several metres of coated fibre. Untreated PET fibres showed a resistivity of around 10^{11} Ω/cm.

It can be seen that, for lower amounts of deposited silver, the measured resistivity was higher compared to the calculated values for ideal coatings, but approached the theory for thicker coatings. Effects such as oxidation at the surface, interface formation between polymer fibre and metal, as well as inhomogeneous coating thickness, are responsible for this finding. In



6.5 Measurement of the resistivity on Ag-coated polyester mono- and multifilament fibres and comparison with theoretically expected values for ideal coatings.

particular for the yarn, some inner filaments were covered and the electric current was mainly conducted by the outer filaments resulting in 'bottle necks' for nano-scaled coatings (<50 nm). Therefore, a coating thickness of around 100 nm is required to obtain a resisitivity of 1 Ω/cm, which is appropriate for good conducting fibres. These Ag-coated fibres are suitable for the development of flexible electrical connections in *smart textiles* and for *wearable computing*. Nano-scaled coatings, however, are adequate to obtain anti-static effects that may be required for medicinal or occupational textiles and electrostatic shielding.

Since thinner coatings can be applied using magnetron sputtering in comparison with electrochemical silver coatings, lower amounts of metal are needed and the textile properties of the fibres remain unaffected. These fibres can thus be processed in a similar manner to uncoated polyester fibres, i.e. Ag-coated textile fabrics can be woven or single Ag-coated fibres can be integrated into a textile fabric with defined spacing. Moreover, in contact with the human skin, silver ions are released from the ultrathin coatings, which reveal a strong anti-bacterial and fungicidal effect.

6.5.3 Scale-up

Due to the low pressures used (<5 Pa), the sputtering of a target material is controlled by the energy and the number of bombarding particles, which gives the corresponding sputtering yield. The process transfer of sputtering with inert gases thus depends on the energy flux to the target, which is mainly determined by electrical and magnetic fields and the plasma power density (power per area) controlling the ionisation degree, while the plasma sheath can be considered as collision-free. Moreover, the geometry of the reactor has to be considered, since the number of collisions between sputtered atoms and the background gas is given by the pressure p and the distance between target and substrate d. Thus, the scale-up of sputtering can be achieved in a first approach by maintaining the number of collisions ($p*d$) and adjusting the power input regarding the area of the treatment (W/cm^2).

6.6 Plasma polymerisation

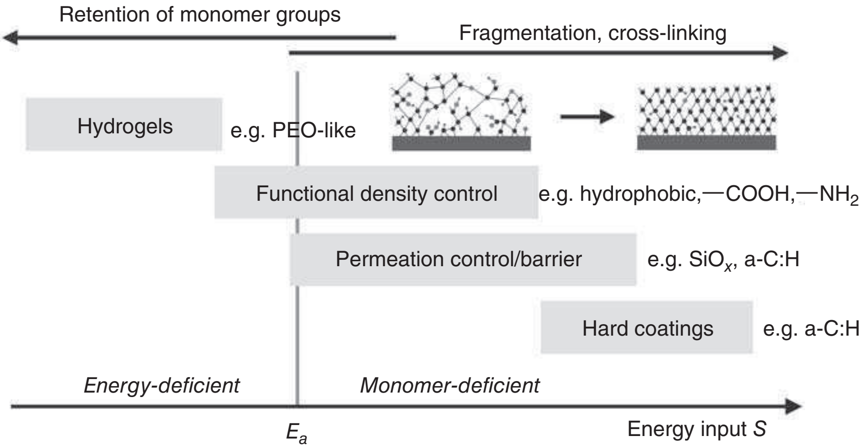
Plasma polymerisation on textiles has gained increasing interest during the last decade, since highly functional surfaces are enabled, resulting in several industrial applications (Hegemann, 2006a). High-value added products with new functionalities such as water/stain repellence, permanent hydrophilicity, dyeability, abrasion resistance, and biocompatibility can be generated due to the nano-scaled modification of fabrics and fibres. At the same time, the bulk properties of the textiles remain unaffected. Moreover, due to the replacement of wet-chemical processes and a low material and energy input, plasma polymerisation provides the realisation of environmentally sound processes.

Plasma polymerisation, which means radical-promoted processes, can be described by the composite parameter power input per gas flow W/F, which relies on the concept of macroscopic kinetics (Rutscher, 1993; Yasuda, 2005). This statistical approach considers the energy invested per particle within the active plasma zone yielding an excited state, such as a radical, and subsequent recombination in a passive zone, yielding a stable product such as a deposition. Hence, the expansion of the plasma has to be taken into account (Hegemann, 2006b). A monomer-dependent activation energy E_a can be derived by evaluating the mass deposition rates R_m (Hegemann, 2001; Hegemann, 2005a) considering that

$$\frac{R_m}{F} = G \exp\left(-\frac{E_a}{W/F}\right) \qquad [6.2]$$

with a reactor-dependent geometrical factor G. An Arrhenius-type plot of Equation [6.2] by variation of W/F parameters gives a straight line, where its slope corresponds to E_a, proving the validity of this approach. Deviations might be found at low and high energies due to oligomers taking part in film growth and energetic particle interactions, respectively (Hegemann, 2005b).

At an energy input below the activation energy, for example, swellable hydrogel films can be deposited such as polyethylene oxide-like coatings (Figure 6.6). By increasing the energy input into the active plasma zone, the



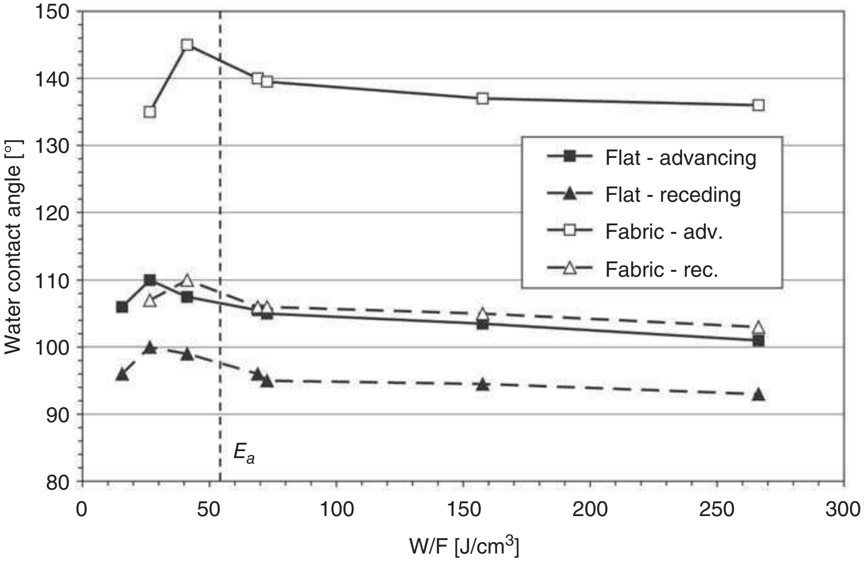
6.6 Different regimes of functionality and cross-linking that can be covered by plasma polymerisation depending on the energy input.

degree of retention of functional groups can be controlled due to enhanced fragmentation at higher energies. Further increase of energy input leads to the formation of dense barrier coatings, when, e.g. hydrocarbons are used as precursors.

6.6.1 Fabrics

Different (low-pressure) plasma polymerisation processes applied to textile fabrics have already been transferred to an industrial level (Hegemann, 2006a). Siloxane coatings derived from organosilicone discharges are used as durable, fluorine-free hydrophobic coatings. Plasma polymers consisting of a Si—O backbone with retained methyl (CH_3) groups yielding low surface energies can be achieved, e.g. by using hexamethyldisiloxane (HMDSO) as monomer. While the hydrophobic properties of pp-HMDSO coatings slightly decrease at increasing energy input, the cross-linking and thus the mechanical properties, can be enhanced (Hegemann, 2001). As shown in Figure 6.7, remarkably higher contact angles can be achieved with structured textile fabrics compared to flat surfaces such as PET foils (Hegemann, 2005d).

The addition of oxygen to HMDSO discharges enables the reduction of hydrocarbon incorporation during film growth, increasing the inorganic



6.7 Plasma polymerised HMDSO coatings used for the hydrophobization of PET fabrics. Due to the textile structure, higher contact angles can be achieved compared with flat surfaces.

character of the coatings and further enhancing the mechanical properties. Thus, abrasion resistant, quartz-like coatings can be deposited on flexible materials when a gradient layer is applied to reduce internal stresses at the interface polymer/coating (Hegemann, 2005a).

Fluorocarbons, on the other hand, are plasma polymerised as stain repellent coatings, showing better durability compared to common wet-chemical treatments (Zhang, 2003). Moreover, textile properties such as feel (touch), optics, and mechanical strength remain unaffected by the nano-scaled plasma polymers covalently bonded to the textile surfaces.

Diamond-like carbon (DLC) coatings deposited on fabrics within hydrocarbon plasmas were investigated for their mechanical, tribological and biological properties (Hauert, 2003). Adhesion on flexible substrates could be enhanced by interfacial gradient layers.

The key factor for plasma polymerisation, however, is given by the add-on value outperforming other available techniques. Examples are tailored plasma polymers containing functional groups to achieve permanent hydrophilic treatments for improved wicking, adhesion and dyeability (Hegemann, 2006a; Hossain, 2006c) or specific binding of linker molecules enabling regioselective treatments on hollow fibres used for blood dialysis (Oehr, 2005).

6.6.2 Fibres

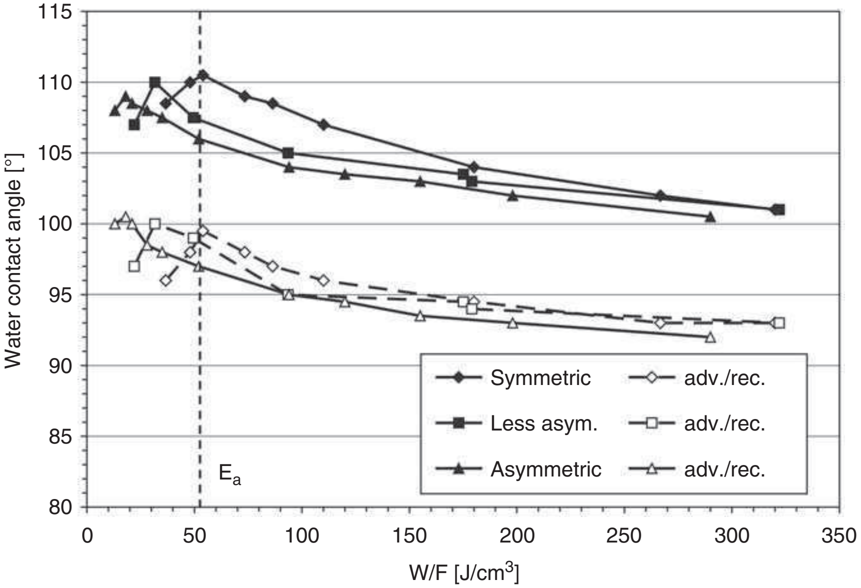
Siloxane coatings using a HMDSO discharge can also be deposited directly on fibres, in a continuous process, to obtain, for example, a hydrophobic, water-repellent yarn. A PET yarn (167 f136) was conducted several times through the deposition chamber of our fibre coater to increase the velocity of the plasma polymerisation process by parallel treatment. An RF antenna was used to activate the glow discharge placed at the centre of the cylindrical vacuum chamber, in parallel to the aligned yarn sections. Regarding the continuous process, each section of the yarn passes different zones of the plasma chamber by moving along the axis and through different radial positions due to the directional change of the yarn. Since the deposition is performed on floating potential to obtain an all-side treatment of the fibres, the deposition rate depends on the luminosity distribution and thus the plasma density of the unconfined plasma around the RF antenna, which was found to decrease with the distance to the antenna after passing a maximum at the plasma/sheath boundary. Thus, varying deposition conditions should be regarded for a continuous plasma polymerisation on fibres. However, we found that the film chemistry (retention of methyl groups and cross-linking) using a HMDSO discharge mainly depends on the energy input by the reaction parameter W/F which is also influenced by pressure, yielding a broader active plasma zone at lower pressures and less on the deposition position within the plasma chamber. Hence, almost constant deposition conditions with respect to film chemistry can be obtained by using a suitable feed-in of the HMDSO monomer. Nano-scaled functional plasma polymers can thus be deposited directly on the fibre geometry within a continuously running process.

6.6.3 Scale-up

The retention of functional groups and the degree of cross-linking of plasma-polymerised films is determined by the absorbed energy (J/cm^3) within the active plasma zone and the interaction of energetic particles during film growth (given by the sheath potential and pressure). Using RF plasma excitation, which enables well-defined deposition conditions with respect to the plasma expansion and power coupling, the influence of energetic particles can be enhanced by reducing the pressure (less collisions within the plasma sheath) or increasing the degree of asymmetry, since smaller RF electrode areas cause higher bias potentials. Therefore, we compared different reactor geometries by performing HMDSO discharges. Regarding the real power absorbed within the active plasma zone (by considering the plasma expansion) and the real flow contributing to film deposition (by considering by-passing of flow) we were recently able to prove that the activation energy of plasma polymerisation derived from mass deposition rates following Equation [6.2], i.e. the plasma chemistry solely depends on the reaction parameter W/F, which can be used for the scale-up (Hegemann, 2005e). For symmetric reactors, the highest recorded water contact angles, which result from the retention of methyl groups during deposition, coincide with the obtained activation energy for HMDSO discharges (Hegemann, 2001). For asymmetric reactors, however, a shift towards lower energy inputs was obtained (Figure 6.8), indicating the increasing influence of energetic particle bombardment. Further increase of the particle bombardment, which can be controlled by the bias potential, leads to rivalling deposition/etching conditions, and the approach of macroscopic kinetics regarding the specific energy W/F fails. After a transition region (above a bias voltage of about 100 V), however, the properties of amorphous hydrocarbon (a-C:H) coatings, for example, can be controlled by the bias potential, which can be used for the up-scaling of DLC coatings (Jacobsohn, 2002; Rangel, 2004).

6.7 Plasma co-polymerisation

Although the field of medical devices has made significant technological advancement, the bacterial colonisation of biomaterials remains a major clinical problem, often leading to device failure, and can be fatal (Vincent,

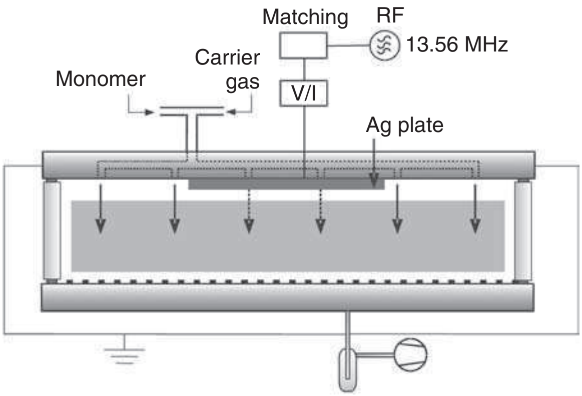


6.8 Advancing and receding water contact angle of plasma-polymerised HMDSO coatings, depending on the energy input and the degree of asymmetry of the RF plasma set-up.

1995). Although the precise mechanism of infection has not been identified, it is well known that the surface properties of biomaterials (e.g. chemistry, wettability and morphology) play an important role in their interaction with the surrounding environment and the success of their application (An, 1998). One of the more effective anti-bacterial methods currently under investigation is based on the design of a coating that contains silver (Balazs, 2004a, 2005a; Davies, 1997; Fox, 1969). The toxic effects of metallic and monovalent silver are bacterial-specific and contact will prove fatal to pathogens containing sulfhydryl functional groups (Davies, 1997). Silver has been proven effective in killing over 650 disease-causing organisms, and is active against gram-negative bacteria, such as *Pseudomonas aeruginosa*, as well as gram-positive bacteria, fungi, protozoa and certain viruses. The 2500-year history of application in water purification has further established the non-toxicity of silver at low concentrations, and Davies and Etris (1997) further describe that monovalent silver is non-toxic to mammalian cells because sulfhydryl (—SH) groups are not exposed on the membranes. However, the cyto-toxicity of Ag is still under scrutiny for certain medical applications (Stickler, 1999). Due to the bacterial-toxic effects of released silver ions (Davies, 1997), it is hypothesised that Ag/plasma polymer films may offer long-term resistance to bacterial adhesion and prevent the colonisation of biomaterial surfaces. Such Ag/plasma polymer nano-composite materials, consisting of nano-scaled metal clusters embedded within a plasma–polymer matrix, can be deposited using a mixed plasma polymerisation/sputtering process (Favia, 2000; Balazs, 2005a). For example, Ag containing plasma polymer nano-composites are deposited employing a silver cathode, an appropriate monomer to yield the desired material properties of the matrix (non-fouling, cell-adhesive, hydrophilicty, etc.) and an asymmetric reactor design, as illustrated in Figure 6.9.

The plasma deposition of nano-Ag/plasma polymer films can be described as a mixed process, including the deposition of a plasma polymer matrix and the sputtering of silver atoms; the sputtering of silver necessitates that the discharge is operated at conditions that favour ion bombardment of the cathode, including lower pressure (*ca.* 0.1 mbar) and higher input power than is commonly used for plasma polymerisation. Unfortunately, such conditions also correspond to a high monomer fragmentation regime, and can result in a decreased functionality of the plasma polymer matrix. Therefore, the deposition of nano-Ag/plasma polymer films can be considered as a compromise between having an acceptable quantity of silver to add an anti-bacterial property, and maintaining enough of the functionality of the matrix in order to confer additional properties of the coatings (Balazs, 2005a). Nano-particle quantity and matrix characteristics of the films can be tailored to specific requirements by altering deposition parameters such as power input, pressure and Ar feed ratio (Balazs, 2005a, b).

Examples of such coatings include Ag/ poly(ethylene-oxide) (PEO)-like (Ag/PEO-like) coatings, which combine the non-fouling properties of conventional PEO materials that hinder the adsorption of proteins and the germicidal properties of silver ions released in media which occurs upon swelling of the hydrogel matrix. Retention of the ether carbon functional-

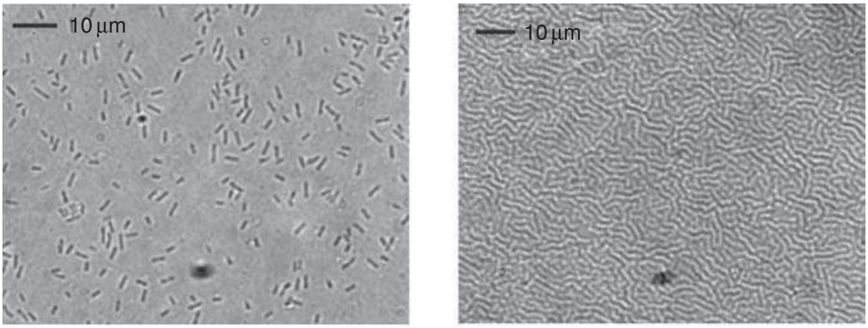


6.9 Schematic representation of the asymmetric plasma reactor used to deposit Ag/plasma polymer nano-composites.

ities in the monomer, often referred to as the 'PEO-character', has been demonstrated to be the determining factor of the non-fouling nature of plasma-deposited PEO-like coatings (Lopez, 1992; Favia, 1998). Despite their reduced PEO character as compared to films produced under low monomer fragmentation conditions, Ag/PEO-like coatings completely prevented the adhesion of four different *P. aeruginosa* strains when deposited on medical grade PVC. The 100% reduction for the PAO1 *P. aeruginosa* strain following Ag/PEO-like coating deposition on PVC is illustrated in Figure 6.10 (Balazs, 2005a). Another example includes Ag/Teflon-like coatings which were also capable of reducing adhesion of a 1.1A1 *P. aeruginosa* strain by 86% and 93% as compared to medical grade PVC and Ag-free Teflon-like thin films (Balazs, 2004b, 2005b). It was demonstrated that increasing the Ag-content, through changes in input power, allowed for an increased reduction in bacterial adhesion.

By changing the target material used at the cathode, this technique also allows for the possibility to include various metallic or ceramic nanoclusters. In addition to silver, some other examples of a nano-composite used in biotechnology are Au-containing Teflon-like (d'Agostino, 1991) and quartz-like coatings (Fracassi, 1996), where the released Au nano-particles were found to specifically bind to cancer cells (El-Sayed, 2005). Ceramic TiO_2 nano-particles might be also of interest as UV-absorbing layer for synthetic fibres, or odor repellent textiles (Wedler, 1999).

In addition to all of the advantages of plasma processing techniques, the formation of metal nano-cluster/plasma polymers by this technique allows for an *in situ* immobilisation of nano-particles that is possible during plasma deposition, providing a one-step coating process that eliminates the



Medical grade PVC

Medical grade PVC +
Ag/PEO-like

6.10 Micrographs illustrating the bacterial adhesion of the PAO1 *P. aeruginosa* strain to medical grade PVC (left) and Ag/PEO-like coatings (right).

necessity of direct handling of nano-particles (Balazs, 2005a; Favia, 2000). Furthermore, through the incorporation of nano-particles in a polymer matrix, it is possible to significantly reduce the amount of metallic material as compared to electrochemical techniques, thus having an important effect on cost, especially when precious metals, such as silver or gold, are considered. This technique allows the possibility to control how much metallic material is incorporated in a coating through changes in particle size.

6.8 Future trends

Low-pressure plasma processes have made inroads even where economic margins are slim, since plasma treatments have unique capabilities and are environmentally benign. Thus, many conventional processes, mainly wet-chemical ones, can be replaced.

The approach to deposit nano-scaled coatings on textiles is of special interest, since textile bulk properties remain unaffected. For example, metallised fibres can be woven under the same conditions as untreated fibres or yarn. Integrating electronics into clothing is an important new concept, which opens up a whole array of multi-functional, wearable electro-textiles for sensing/monitoring body functions, delivering communication facilities, data transfer, individual environment control, and many other applications (Tao, 2005).

Controlled drug delivery is an important development in biotechnology, where plasma processing allows for the production of novel substrates with tight control of polymer cross-linking and release rates upon swelling. The production of multi-layer, gradient and reservoir systems which are difficult to achieve by wet chemical techniques are greatly facilitated by plasma processing. Smart textiles that enhance wound healing, prevent infection or provide feedback to physiological responses will be important product developments for human well-being.

Hydrophobic and oleophobic coatings are still of high interest, since wet-chemical treatments reveal a lack of sufficient washing fastness. Thus, cross-linked plasma coatings should further be examined. The same holds for permanent hydrophilic coatings, where new types of nano-scaled functional plasma coatings that show reduced ageing and enhanced washing fastness are currently under investigation.

Hence, textile trends that are relevant for plasma treatments deal mainly with hydrophobic/oleophobic, hydrophilic functional, anti-static and conductive, anti-microbial and medicinal coatings, as well as multi-functional surfaces. A further trend will lead to strong, thermally stable and highly abrasion-resistant textiles, where plasma technology will also have a contribution. Besides functionality, the comfort of functional textiles for the user becomes more and more a main focus.

6.9 Sources of further information

Wearable Electronics and Photonics (Woodhead Publishing, 2005) edited by X. M. Tao (Hong Kong Polytechnic University) shows the major new concepts of integrating electronics into clothing and explores future trends for fashion and specialist clothing. Surface properties of textiles, which are relevant for plasma treatments, are covered by C.M. Pastor and P. Kiekens *Surface Characteristics of Fibers and Textiles* (Marcel Dekker, 2001). A comprehensive overview of sputter deposition is given by W. Westwood in *Sputter Deposition* (AVS Education Committee Book Series, Vol. 2, 2003). Plasma polymerisation is extensively treated by H. Yasuda in his new book *Luminous Chemical Vapor Deposition and Interface Engineering* (Marcel Dekker, 2005). Industrial-size plasma reactors are delivered, for example, by Europlasma (www.europlasma.be) or Sigma Technologies International (www.sigmalabs.com). Know-how in continuous plasma deposition and reactor development can further be used, e.g. from Plasma Finish (plasma polymerisation; www.plasma-finish.com), Von Ardenne Anlagentechnik (sputtering; www.vaat.biz) and Roth & Rau (fibre coating; www.roth-rau.de).

Empa's activities within its Department 'Materials and Systems for Protection and Wellbeing of the Human Body' can be looked up at www.empa.ch.

6.10 References

Amberg M, Geerk J, Keller M, Fischer A (2004), 'Design, characterization and operation of an inverted cylindrical magnetron for metal deposition', *Plasma Devices Operations*, **12**, 175–186.

An Y H, Friedman R J (1998), 'Concise review of mechanisms of bacterial adhesion to biomaterial surfaces', *J Biomed Materials Res: Applied Biomaterials*, **43**, 338–348.

Balazs D J, Triandafillu K, Wood P, Chevolot Y, van Delden C, Harms H, Hollenstein C, Mathieu H J (2004a), 'Inhibition of bacterial adhesion on PVC endotracheal tubes by RF–oxygen glow discharge, sodium hydroxide and silver nitrate treatments', *Biomaterial*, **25**, 2139–2151.

Balazs D J, Triandafillu K, Strahm B, Dorier J L, Hollenstein C, Mathieu HJ (2004b), 'PE-CVD modification of medical grade PVC to reduce *Pseudomonas aeruginosa* adhesion: nano-composite Ag/Teflon-like coatings' *PSE 2004 Proceedings, Garmisch-Partkirchen*, VDI Technologiezentrum, 62.

Balazs D J, Triandafillu K, Sardella E, Iacoviello G, Favia P, d'Agostino R, Harms H, Mathieu H J (2005a), 'PE-CVD modification of medical grade PVC to inhibit bacterial adhesion: PEO-like and nano-composite Ag/PEO-like coatings' in d'Agostino R, Favia P, Oehr C and Wertheimer M R (Eds), *Plasma Processes and Polymers*, Wiley-VCH, Weinheim, 351–372.

Balazs D J, Hollenstein C, Mathieu H J (2005b), ‘Fluoropolymer coating of medical grade poly(vinyl chloride) by plasma-enhanced chemical vapor deposition techniques’, *Plasma Process Polym*, **2**, 104–111.

Castelvetro V, Fatarella E, Corsi L, Giaiacopi S, Ciardelli G (2006), ‘Graft polymerisation of functional acrylic monomers onto cotton fibres activated by continuous Ar plasma’, *Plasma Process Polym*, **3**, 48–57.

d’Agostino R, Martinu L, Pische V (1991), *Plasma Chem Plasma Proc*, **11**, 1.

Davies R L, Etris S F (1997), ‘The development and functions of silver in water purification and disease control’, *Catalysis Today*, **36**, 107–114.

El-Sayed I H, Huang X, El-Sayed M A (2005), ‘Surface plasmon resonance scattering and absorption of anti-EGFR antibody conjugated gold nanoparticles in cancer diagnostics: Applications in oral cancer’, *Nano Lett*, **5**, 829–834.

Favia P, d’Agostino R (1998), ‘Plasma treatments and plasma deposition of polymers for biomedical applications’, *Surf Coat Technol*, **98**, 1102–1106.

Favia P, Vulpio M, Marino R, d’ Agostino R, Mota R P, Catalano M (2000), ‘Plasma-deposition of Ag-containing polyethyleneoxide-like coatings’, *Plasmas Polym*, **5**, 1–14.

Fox C L, Rappole B W, Stanford W (1969), ‘Control of Pseudomonas infection in burns by silver sulfadiazine,’ *Surgery, Gynecology and Obstetrics*, **128**, 1021.

Fracassi F, d’Agostino R, Palumbo F, Bellucci F, Monetta T (1996), ‘Deposition of gold-containing siloxane thin films’, *Thin Solid Films*, **272**, 60–63.

Hauert R, Müller U (2003), ‘An overview on tailored tribological and biological behavior of diamond-like carbon’, *Diam Rel Mater*, **12**, 171–177.

Hegemann D, Brunner H, Oehr C (2001), ‘Plasma treatment of polymers to generate stable, hydrophobic surfaces’, *Plasma Polym*, **6**, 221–235.

Hegemann D, Oehr C, Fischer A (2005a), ‘Design of functional coatings’, *J Vac Sci Technol A*, **23**, 5–11.

Hegemann D, Hossain M M (2005b), ‘Influence of non-polymerizable gases added during plasma polymerization’, *Plasma Process Polym*, **2**, 554–562.

Hegemann D (2005c), ‘Stain repellent finishing on fabrics’, *Adv Eng Mater*, **7**, 401–404.

Hegemann D (2005d), ‘Plasma functionalization of textiles and fibers’, in M Mutlu (Ed.), *Plasma Polymers and Related Materials*, University Press, Ankara, 191–203.

Hegemann D (2005e), ‘Macroscopic plasma-chemical approach to plasma polymerization of HMDSO and CH_4’, *Surf Coat Technol*, **200**, 458–462.

Hegemann D (2006a), ‘Plasma polymerization and its application in textiles’, *Indian J Fibre Textile Res*, **31**, 99–115.

Hegemann D (2006b), ‘Influence of pressure on an asymmetric, radio frequency discharge with methane’, *Thin Solid Films*, in press.

Hossain M M, Hegemann D, Herrmann A S, Chabrecek P (2006a), ‘Contact angle determination on plasma-treated poly(ethylene terephthalate) fabrics and foils’, *J Appl Polym Sci*, **102**, 1452–1458.

Hossain M M, Herrmann A S, Hegemann D (2006b), ‘Plasma hydrophilization effect on different textile structures’, *Plasma Process Polym*, **3**, 299–307.

Hossain M M, Herrmann A S, Hegemann D (2006c), ‘Incorporation of accessible functionalities in nanoscaled coatings on textiles characterized by coloration’, *Plasma Process. Polym.*, in press.

Jacobsohn L G, Capote G, Cruz N C, Zanatta A R, Freire F L, Jr (2002), 'Plasma deposition of amorphous carbon films from CH_4 atmospheres highly diluted in Ar', *Thin Solid Films*, **419**, 46–53.

Kang, J-Y, Sarmadi M (2004a), 'Textile plasma treatment review – natural polymer-based textiles', *AATCC Rev*, **10**, 28–32.

Kang, J-Y, Sarmadi M (2004b), 'Textile plasma treatment review – synthetic polymer-based textiles', *AATCC Rev*, **11**, 29–33.

Keller M, Ritter A, Reimann P, Thommen V, Fischer A, Hegemann D (2005), 'Comparative study of plasma-induced and wet-chemical cleaning of synthetic fibers', *Surf Coat Technol*, **200**, 1045–1050.

Kersten H, Deutsch H, Steffen H, Kroesen G M W, Hippler R (2001), 'The energy balance at substrate surfaces during plasma processing', *Vacuum*, **63**, 385–431.

Kull K R, Steen M L, Fisher E R (2005), 'Surface modification with nitrogen-containing plasmas to produce hydrophilic, low-fouling membranes', *J Membrane Sci*, **246**, 203–215.

Liston E M, Wertheimer M R (1993), 'Plasma surface modification of polymers for improved adhesion: a critical review', *J Adhesion Sci Technol*, **7**, 1091–1127.

Lopez G P, Ratner B D, Tidwell C D, Haycox C L, Rapoza R J, Horbett, T A (1992), 'Glow discharge plasma deposition of tetraethylene glycol dimethyl ether for fouling-resistant biomaterial surfaces', *J Biomed Materials Res*, **26**, 415–439.

Oehr C, Hegemann D, Müller M, Vohrer U, Storr M (2005), 'RF-plasma treatment on the inside of small functional devices for biomedical application', in d'Agostino R, Favia P, Oehr C and Wertheimer M R (Eds), *Plasma Processes and Polymers*, Wiley-VCH, Weinheim, 309–317.

Poll H U, Schladitz U, Schreiter S (2001), 'Penetration of plasma effects into textile structures', *Surf Coat Technol*, 142–144, 489–493.

Rangel E C, da Cruz N C, Kayama M E, Rangel R C C, Marins N, Durrant S F (2004), 'Optical and electrical properties of polymerizing plasmas and their correlation with DLC film properties', *Plasmas Polym*, **9**, 1–22.

Rossnagel S M (2003), 'Thin film deposition with physical vapour deposition and related technologies', *J Vac Sci Technol A*, **21**, S74–S87.

Rutscher A, Wagner H-E (1993), 'Chemical quasi-equilibria: a new concept in the description of reactive plasmas', *Plasma Sources Sci Technol*, **2**, 279–288.

Stickler D J (1999), 'Biomaterials to prevent nosocomial infections: is silver the gold standard?' *Current Opinion in Biotechnology*, **13**, 389–393.

Tao X M (2005), *Wearable Electronics and Photonics*, Woodhead Publishing, Cambridge.

Vincent J L, Bihari D J, Suter P M, Bruining H A, White J, Nicolas-Chanoin M H, Wolff M, Spencer R C, Hemmer M (1995), 'The prevalence of nosocomial infection in intensive care units in Europe. Results of the European Prevalence of Infection in Intensive Care (EPIC) Study', *Journal of the American Medical Association*, **274**, 639–644.

Wedler M, Hirthe B (1999), *Chem Fibers Int*, **49**, 528.

Wertheimer M R, Fozza A C, Holländer A (1999), 'Industrial processing of polymers by low-pressure plasmas: the role of VUV radiation', *Nucl Instr Meth Phys Res B*, **151**, 65–75.

Yasuda H (2005), *Luminous Chemical Vapor Deposition and Interface Engineering*, Marcel Dekker, New York.

Zhang J, France P, Radomyselskiy A, Datta S, Zhao J, van Ooij W (2003), 'Hydrophobic cotton fabric coated by a thin nanoparticulate plasma film', *J Appl Polym Sci*, **88**, 1473–1481.

Part II

Textile applications

7

Plasma treatment of textiles for water and oil repellency

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P2i Ltd, UK

7.1 Introduction

Most liquid-repellent textile treatments are simply treatments exclusively for textiles and are often specific to individual textiles. It would be a great advantage if the same levels of liquid repellency could be applied to a multitude of textiles and materials, independent of composition, with the added benefit of being able to apply it to the final product. Plasma technology allows this to be realised, where one of the main features is the ability to place the entire end product into the chamber and render all components liquid repellent, i.e. not just the textile or material but the zips, seams and fasteners, protecting the whole item from liquids. This benefit extends into all market areas, where the end product can undergo the plasma enhancement process to provide the liquid-repellent properties.

Many chosen materials in products all around us are selected either for their bulk physical properties or ease of processing. However, their resulting surface properties can be far from ideal for their intended use. Plasma processing allows the surface properties, typically from angstroms (10^{-10} m) to 10s–100s of nanometres (10^{-9} m) in thickness, to be further optimised, without affecting the bulk properties, and allowing the product to perform at a much higher level in its intended application and often opening up new applications altogether. It is desirable to offer high levels of water and oil repellency, especially for adverse weather conditions and proximity of textiles to liquids, such as food and beverages that can easily come into contact with items of clothing and furnishings.

This chapter considers the requirement for water and oil repellency for textiles and looks at the features and benefits, along with the critical factors of a diverse number of products in a number of industry sectors (Section 7.2). The theory and testing of water and oil repellency is explained in Section 7.3 with current solutions for rendering textiles water and oil repellent being covered in Section 7.4. The use of plasmas for imparting liquid repellency is address by a case study of the scale-up issues faced with commercialising a low-pressure plasma process for imparting water and oil repellency (Section 7.5), which also touches on some of the background work on the use of plasmas to achieve this technical effect. Finally Section 7.6 covers what the future holds and outlines a vision for plasma processing and important milestones that need to be achieved for the technology to be commercially acceptable. A list of useful references where further information can be sought, in addition to the details of where much of the information has been sourced, is cited in Section 7.7.

7.2 Requirement for water and oil repellency

7.2.1 Providing added value

Customers demand increasing functionality from products they buy. Examples include something as complicated as greater resolution on medical instrumentation, as demanding as temperature tolerances of solar panels on space shuttles, or simply a longer lasting filter for their car or a suit that does not get wet when it rains. People either want more for their money or are willing to pay for the benefits of a differentiated product. Either way, if a company wants to become successful by delivering a more cost-effective solution or increasing market share, it must innovate and provide value-added solutions. This value-added feature can be far ranging, from a tangible differentiator such as a new colour or technical effect, to a less tangible factor such as use of an environmentally friendly process. This section will concentrate on the tangible benefits of added technical effects.

All products around us have several things in common:

- They are generally made of more than one material, such as plastics, textiles, glass, ceramics, metals, rubbers, wood
- They require the assembly of smaller components or raw materials in order to become a usable product
- They will come into contact with different environments throughout their life-time, such as various liquids, temperatures and abrasive conditions and
- The performance properties required of the product may be very different from those of the raw materials selected to make the components of the product.

To expand on the last point, materials will be chosen for many different factors, such as cost, ease of processing, historical reasons or performance requirements. In most cases, the materials chosen will not only give rise to the bulk properties but also the surface properties, and for many products it is the interaction with the surface that either dictates the performance or is a very effective way of adding considerable value through a differentiating technical effect. For many devices, an optimum solution would be to process using cheap, well-known, manufacturing-friendly materials and then modify the surface using an additional process to impart whatever functionality is required.

Many added-value technical effects are available, such as flame retardency, antimicrobial properties, ability to conduct electricity or thermal energy, anti-corrosion, anti-smear, anti-fogging, protein resistance, hydrophilicity, haema compatibility, oil and water repellency: and this is far from an exhaustive list. Many of these properties are already available; however, it may only be possible to apply them to a small number of materials due to limitations with processing techniques. What the majority do have in common is a durable surface application that is product specific. It is often not necessary to apply the technical effect throughout the bulk of the materials used to make up that product. This presents interesting opportunities for adding value to textiles using a universal surface modification technique.

7.2.2 Focus on water and oil repellency

Liquid repellency is a wide-reaching technical effect that is sought after in several industry sectors, from biosciences, healthcare and electronics to industrial filtration, sports and active wear. Often, repellency to water alone is not enough and other liquids such as oils, inks and alcohols need to be repelled. Liquids are constantly in use around us, in the majority of cases in the form of rain water and food and beverages. Arguably, the most noticeable, unfavourable interactions of these are with textile products such as clothing, carpets and upholstery, so added value can be provided by simply protecting these items from interacting with the liquids, enabling the liquids to roll off or be dabbed away, leaving the underlying material unchanged. The theory behind this will be covered in detail in Section 7.3.

Providing liquid repellency to textiles has always been a desirable effect as very few are inherently liquid repellent and the variety of substrates possible has led to many different methods of applying the technical effect; this will be covered in some detail in Section 7.4. By breaking down the different industry sectors into products, features and benefits of liquid repellent properties, an idea of why liquid repellency is so far reaching for textile applications can be illustrated (Table 7.1). Examples of some of the required critical factors are also included in the table.

Although more simply termed water and oil repellency, the description covers repellency of many other liquids including inks and alcohols. Further challenges are presented when more viscous liquids or solid/liquid slurries containing reactive dyes and acids come into contact with a material, due

Table 7.1 Breakdown, by industry sector, of product benefits and critical factors of liquid repellent treatments of textiles

Industry sector	Example products	Features/Benefits	Critical factors
Medical	• Bandages	• Prevents both water ingress and blood/ ointment wicking • Less pain for patient or chance of rupture when detaching from wound	• No cytotoxicity or leachables
Electronics	• Fuel cells	• Reduces liquid transport • Increases battery lifetime • Ability to harbour more power	• Provide robust effect that is not easily broken down
Automotive and aerospace	• Seat covers	• Minimises staining – fresh look for longer • Minimises odour and smoke uptake – improved hygiene • Easy clean	• Durability for product life-time • Product often a complex 3D shape • Can it be re-processed?
Fashion	• Designer shoes, bags and clothing	• Retains desired look and colours for longer, as often not possible to clean due to material or design selection	• Must not impair aesthetics or hand; no perceivable change is acceptable
Sports and active wear	• Trainers • Lightweight jackets	• Waterproof performance with minimal heat stress • Rain protection in lightweight garments • Wearer stays dry and garment remains light	• Maximised performance for product life-time • Wash durability
Military	• Military warfare clothing	• Resists chemical agent challenges such as nerve agents and mustard gas, in addition to environmental challenges such as rain water	• Very low surface energies required • Often need to include many different technical effects into as few a layers as possible • Durability requirements need to be met

to the rheology or reactive nature. It is not the intention to discuss this in detail, as they are covered in great depth in other texts, but to concentrate more on the general requirements of repellency.

7.3 Theory and testing of water and oil repellency

7.3.1 Surface energy and surface tension

The science of liquid repellency is often overlooked. Generally speaking, the phenomenon relies on three main aspects:

- surface energy of the base material
- surface energy of the coated material
- surface tension of the liquid in contact with the surface.

Although there are other contributing factors, just the interactions of solids with liquids will be addressed for the purpose of this discussion.

Repellency in itself is a confusing term as this is often perceived as forcing something away, in the way that like magnetic poles repel each other. The majority of liquid repellents do not 'force' the liquid away, but merely present an inert surface where fewer interactions take place. Having said this, the term repellency will be used to describe this phenomenon due to its popular acceptance.

All solid surfaces have surface energy, which is a function of surface area and the amount of electronic charge present, made up by the molecules at that surface. In addition, all liquids have a surface tension, which is a measure of the interaction energies between the molecules that make up that liquid when at the gas/liquid interface. The most common units used to measure surface energy and surface tension are dynes/cm and mN/m, i.e. force per unit length which is analogous to energy per unit area.

Liquids such as water have a high surface tension due to the strong interactions between the polar water molecules. At the air/water interface, this interaction energy is exhibited by the surface molecules displaying a 'skin' like effect. Oils have low surface tensions as there are only very weak interactions between the apolar molecules.

All liquids, as is common with many things in nature, wish to attain the minimum energy state possible and are mobile enough to do that. They will move to minimise the interfacial tension between themselves and the environment they are in. What this means in practice is that, for a pure liquid suspended in mid air, providing there are no external forces, the shape adopted to minimise the interfacial tension is that of a sphere, i.e. the geometric shape where the maximum number of molecules are in contact with each other. As external energy is provided, such as a surface, the shape will adjust to minimise the new interfacial energy.

Water has one of the highest surface tensions of common liquids around us, with a value of ~72 mN/m at 20°C. It should be noted here that surface tension and surface energy are a function of temperature, and they will increase as temperature increases. Generally speaking, high surface tension liquids will sit with high contact angles on a low surface energy material; for example, a droplet of water on a freshly waxed car. Conversely, low surface tension liquids will sit with low contact angles on high surface energy materials, for example, olive oil in a metal frying pan.

In reality, few surfaces are truly flat, and especially so in the textile world. It is important to understand how the surface roughness affects the interactions between the liquid and the material contacting and this will help explain why textiles are adversely affected by liquids.

7.3.2 Surface roughness

Surface roughness will enhance the repellency effects seen on a flat surface of the same chemical composition. Generally speaking, and taking water as an example, if a droplet of water is in contact with a flat material and has a contact angle greater than 90º, then if the surface is roughened, the contact angle will increase, displaying super hydrophobicity. The material is said to be inherently hydrophobic and less energy is required to move the droplet across the surface (Figure 7.1). Conversely, if the droplet of water is less than 90º on a surface, then the material is inherently hydrophilic, and roughening the surface will result in a lower contact angle, as greater interaction energy results (Figure 7.2).

7.3.3 Achieving liquid repellency

As described earlier, many materials do not display the surface properties required for a particular product to function as required and there is a need

7.1 Super hydrophobicity resulting from surface roughening of a hydrophobic surface.

7.2 Effect of surface roughening of a hydrophilic surface.

to change these properties in order to give the product a much wider scope of use. Very few textiles are inherently water repellent and none are oil repellent. Therefore, an additional process must be added to display these properties. This process can be any one of a number of techniques which will be discussed in greater detail in Section 7.4. All the techniques apply lower surface energy chemical groups to the surface in order to reduce the interaction energies. The main three chemicals used to deliver these groups are hydrocarbons, silicones and fluorocarbons, which can be used alone or in combination.

Hydrocarbon and silicone based repellents only repel water, so if oil repellency is required, fluorocarbons have to be used to some degree. Fluorocarbons are far more expensive than hydrocarbons, especially when used in large quantities, which is why they are often co-applied. Finding techniques for reducing the amount of fluorocarbon used, whilst still retaining the high levels of repellency, are much sought after.

Fluorocarbons have the potential to reduce the surface energy to the lowest values possible, where the long fluorinated chains of the chemical attach normal to the surface of the substrate. The repellency of the resultant finish depends on several factors such as the fluorinated and nonfluorinated segments, the orientation, the distribution of the fluorocarbon groups on the fibres and the composition and geometry of the fabric.

7.3.4 Testing water and oil repellency

Not surprisingly, there are numerous ways of measuring liquid repellency. Many of these have been developed by companies in order to deliver the specific product requirements their customers demand. Depending on the product and application, several testing methodologies may need to be applied to demonstrate that the right performance characteristics are delivered.

Table 7.2 lists some of the more popular water repellency tests that are available. These fall into three main categories: (i) spray tests, (ii) hydrostatic pressure tests and (iii) sorption of water tests.

Many requirements for fabric treatments state that air permeability properties need to be retained in addition to the ‘hand’ and ‘drape’ qualities. In these instances tests such as air permeability and water vapour permeability (ASTM D 737-96; DIN 53 887) are also required.

The main oil and water repellency tests for semi-quantitative measurements of surface energy involve placing three small droplets of graded test liquids onto the fabric surface, usually for 30 seconds for oil-based and 10 seconds for aqueous-based liquids. The droplets are removed using an absorptive tissue. If no wetting is observed on the fabric from two out of the three droplets, the next test liquid is used, and so on until wetting is observed. The highest value test liquid used where no wetting is observed

Table 7.2 Commonly-used water repellent tests for treated textiles

Name	Test	Comments
Spray test	AATCC 22-1996	Developed by DuPont Co. Can be carried out without destroying the article. Difficult to differentiate fabrics with good water repellency
Sputter apparatus	AATCC 21-1998	The lowest hydrostatic head needed to cause penetration is recorded. Normally used for fabrics coated with an impermeable film
Dynamic absorption	AATCC 70-1997	Measures weight increase as a percent of water absorbed

Table 7.3 Test liquids for oil repellency ratings

Oil-repellency rating	Test liquid	Surface tension (mN/m)*
1	Nujol oil	31.2
2	65/35 nujol/n-hexadecane	28.7
3	n-hexadecane	27.1
4	n-tetradecane	26.1
5	n-dodecane	25.1
6	n-decane	23.5
7	n-octane	21.3
8	n-heptane	19.7

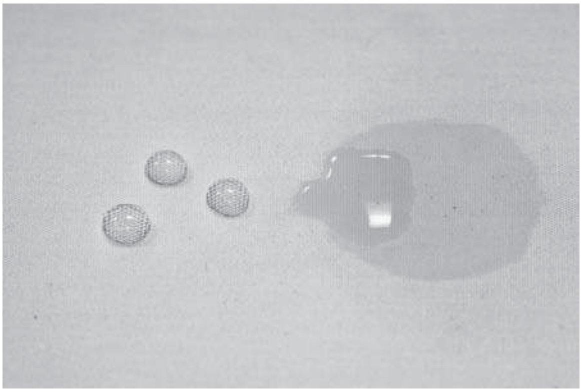
*Data by R. H. Dettre.

is the value given to the textile. The example shown opposite (Figure 7.3) is for the AATCC 118-1997 test method where the *oil* series of liquids ranges from Oil 1 (O1) – Oil 8 (O8), where O1 has the highest surface tension and O8 has the lowest, i.e. the easiest to repel and the hardest to repel, respectively (Table 7.3). As can be seen from the image, the value given to this material is O6. The range of *polar* test liquids are from W0 (100% water) to W10 (100% isopropyl alcohol), where W6 is composed of 60% isopropyl alcohol and 40% water. If the test sample fails the lowest water or oil repellency tests, a value of WF and OF can be recorded, respectively.

7.4 Current solutions for rendering textiles water and oil repellent

7.4.1 Introduction

Treatments for rendering textiles water repellent have been around for many years and the earliest involved using hydrophobic substances such as



7.3 Droplets of decane and octane on a fluorocarbon-treated fabric.

paraffin. Mixtures of wax or paraffin emulsions containing aluminium acetate have also been used. However, as explained earlier, in order to achieve both water and oil repellency, it is necessary to use fluorocarbon moieties.

The terms encountered when describing liquid protection for textiles are ones such as 'waterproof', 'water resistant' and 'water repellent'. All mean subtly different things, which can confuse consumers, and so below is a review of the more popular descriptions and what they actually mean.

Firstly, it should be noted that water, in one form or another, can penetrate most things; it is even used to cut blocks of steel. The determining factor is the pressure applied. To cut a block of steel using water jets requires a pressure of around 60 000 pounds per square inch (psi). Water in this form will rarely be encountered but it serves to show that, providing the force is high enough, water will break through virtually anything. Despite this, the term waterproof is often used where quite simply this refers to liquid protection that is fit-for-purpose. This means that a garment worn containing waterproof technology would expect to stay dry if subjected to the harshest driving rain or if the wearer sat down or knelt in water. The technology will protect you from the force of water likely to be encountered in that situation. Therefore, it can be agreed that different products would require different levels of waterproof-ness depending on the market demands. Water repellent refers to surfaces where water will not wet; however, providing the forces are great enough, they could drive the droplet through the material and the waterproof-ness is therefore a function of the porosity of the underlying material. Water resistant is another confused term and will be used by some industries to describe a surface that is not fully waterproof.

There are many potential situations where people expect to stay dry when the force of water is not very high; however, the product used will still be perceived to be waterproof. For example, running shoes take the majority of the force impact from water with the sole, which is impermeable. So, if running through a shallow stream or puddle, the fall-back of water onto the permeable upper material will have much less force and may not penetrate the shoe, which will therefore be perceived by the wearer as being waterproof.

The main issues of providing fit-for-purpose liquid protection comes down to a compromise between the level of protection provided and the physiological burden imposed. This means it is very easy to provide complete liquid protection to a person. However, the solution would involve completely dressing the wearer head-to-toe in a rubber suit; totally impractical as the wearer will soon tire and become unable to carry on due to the heat stress imposed. By providing just enough protection, greater wear comfort can be achieved, due to the greater breathability of the material. This leads to the necessity to fully segment a particular market to deliver what is required. For example, clothing suitable for harsh weather conditions will be more then likely inappropriate for brief periods of shower resistance, where a more suitable lower physiological burden garment can be provided.

Generally, waterproof fabrics are created by laminating a microporous, or hydrophilic polymer at the backside of the fabric. The reason being, the majority of fabrics are air permeable due to the nature of the weave which allows the desirable drape qualities as well as breathability. A consequence of this is that water can be forced through and so extra protection is required. For many applications where high performance is not required, i.e. no need to protect against a high *force* of water, more open weave structures can be used which are generally more desirable anyway, due to greater breathability which allows any heat and water vapour created by the body to readily pass out of the garment and cool the person wearing it.

There are numerous methods on the market for rendering textiles water and oil repellent, the majority coming under the general description of dip coating and spray coating. They are often referred to as DWRs (durable water repellents). The general consensus seems to be that there is no PWR (permanent water repellent) treatment that can be applied to products, as properties drop off over time, with laundry washing and/or dry cleaning.

7.4.2 Dip processing

The vast majority of processes fall under dip/solution-based coatings and have several factors in common:

- Process is applied to the textile in roll format before construction of the garment or end product
- Vats of complex chemical formulations are used, which not only contain the chemicals required on the textile to give the repellent effects, but many others required to allow the chemical to film-form and attach to the surface
- The vats used are of a particular formulation to attach specific chemical groups onto the textile, so other formulations are required to attach to different types of materials
- High temperatures are required to effect fixation, secure the groups on the surface and drive off the water/solvent required to apply the technical effect.

There are many different companies that provide their own trademarked formulations to achieve this effect and there are specific advantages and disadvantages of these forms of processing:

Advantages

- High through-puts available
- Cost-effective when processing in large quantities
- High levels of liquid repellency possible.

Disadvantages

- Not applied to the end product, therefore complete protection of the constructed product is not possible
- Expensive/unfeasible for small batches
- Cannot be applied to 3D forms and limited to textiles of specific chemical make-up
- Cannot be used as a re-coating process for the end product due to unfavourable solution energetics and incompatibility of product form.

7.4.3 Spray coatings

Again, a wide variety of products are available in the market place providing a range of both water and or oil repellency treatments. The general form of application is through an aerosol-can and, while good levels of protection can be provided, the main issues surround the durability of the treatment along with how much coverage has occurred and the amount of chemical that is lost into the environment.

There are many applications where solution-based dip or spray application is the most economical and present the best method of providing both water and oil repellency. However, like any technique there are inherent drawbacks, and it is because of these that people have looked to alternative technologies that overcome these drawbacks and indeed become benefits of the new process.

7.5 Use of plasmas for imparting liquid repellency

7.5.1 Introduction

As discussed earlier, there are some good advantages to using solution-based applications to render items liquid repellent, but due to inherent drawbacks, alternative technologies are being looked at and indeed have proven cost-effective in many industries where products processed via these new methods are being sold today.

One common problem of solution-based applications is the cost implications of heating vats of aqueous liquids to high temperatures, carrying out the fabric treatment and then using further energy to dry out the fabrics. Due to the general reluctance of using solvents for applying the technical effect and the cost implications of using aqueous based systems, a move away from solution-based processing is very attractive. However, the applicability of new technologies and the cost/performance relationship should be fully understood before embarking on large scale production. One such alternative would be the use of gas phase processing, which eliminates the requirement of having to remove a liquid post-treatment, in addition to numerous other benefits.

The first major challenge, which defines the type of gas phase process, is deciding how to activate the gas phase in order to create a reactive medium that can be used to treat the material of interest. One of the more common methods of activating a gas is through ionisation which produces what is more commonly known as the fourth state of matter and was referred to as a plasma back in 1929 by Langmuir.

7.5.2 Types of plasma

The most common methods of creating a plasma are corona discharge or dielectric barrier discharge, flame treatment and low pressure glow discharge; this is by no means an exhaustive list and the terminology is often confused. The techniques can be broadly broken down into two categories, atmospheric-pressure plasmas and low-pressure plasmas, and these will be addressed separately.

7.5.3 Atmospheric-pressure plasmas

One of the main attractions is undoubtedly the fast line speeds that are potentially possible. Providing the same technical effects can be achieved, in comparison to solution based processing, several advantages of plasma processing exist:

- High line speeds possible, leading to reduced unit cost
- Reduced equipment foot print, as vertical processing is possible
- Minimal environmental impact due to no large chemical vats required
- Can functionalise a wide variety of materials.

However, due to the nature of these processes, items are limited to flat sheets, webs and films that can be processed roll-to-roll and, in general, the final product will not be treated. While this is not always a drawback, it makes atmospheric-pressure plasma processes direct competitors to the solution based application methods. Because of this, the performance/cost relationships can be directly compared to address the feasibility of atmospheric-pressure treatment of textiles for water and oil repellency.

One of the main problems arising through atmospheric-pressure based processing used to obtain water and oil repellency, and indeed other functional effects, is the ability to retain the long chemical chains necessary to give the technical effect. Plasmas are inherently a destructive process and sophisticated processing is required to retain complex chemical groups. In addition, obtaining the required technical effect whilst achieving high line speeds is also a critical calculation in assessing the feasibility. Within the textile industry, fabric functionalisation is low down the value chain so costs need to be at a minimum and equipment sited with the relevant textile manufacturer or distribution warehouse. Another consideration is the management of waste materials that could contain toxic components. Atmospheric plasma processing is covered in Chapters 4 and 5 and these should be consulted for more in-depth information.

7.5.4 Low-pressure plasmas

Introduction

The information contained within this section outlines the benefits of low-pressure plasma processing, specifically addressing the experience encountered with the development of a process and the scale-up of a technology for making textiles water and oil repellent. It does not give an account of low-pressure plasma processing itself as this is covered in detail in Chapter 3. It will address the main challenges faced by scaling-up and providing a cost-effective, value-adding industrial process.

Background

The majority of low-pressure plasma processing systems are batch processes. There are a number of examples where continuous roll-to-roll processing is carried out within a batch process, i.e. there is down-time when changing between rolls as the whole roll is pumped down to low pressure, and a few examples where fully continuous processing is possible through 'whistling leaks' where differentially pumped systems allow the constant transport of material. Batch processing is also possible on a continuous basis or on an in-line system, where samples can be loaded whilst pump down and processing occurs in other sections. Nevertheless, compared with continuous treatment with atmospheric-pressure plasma processing, the line speeds and initial capital costs initially appear unattractive. However, experience has shown that there are numerous technical benefits of operating at low-pressure, where even relatively modest through-puts can provide a cost-effective solution – provided that the technical effect adds sufficient value. The main features of processing at low-pressure are:

- Ability to treat complex 3D items including finished products and off-the-shelf items
- Items can be re-treated if necessary
- Process can be sited anywhere, can easily be integrated into a production line and can be applied anywhere along the value chain
- Process can treat a wide range of different materials at once
- Process gives greater control of the degree of ionisation and hence fragmentation of the starting material. This way raw chemical functional groups can be preserved and attached to the product
- Low amounts of starting raw chemicals are required. Not only does this lead to cheaper processing costs but negligible waste costs and environmental impact
- Depending on the items to be treated, fast through-puts can be possible by simply optimising the system for a particular product.

Nobody expects one process to be best for every application and volume demand; however, it is because of these features that it is believed low-pressure plasma processing can deliver considerable value to a wide number of products in numerous market areas.

Process development

Conventionally, low-pressure plasmas have been used as a means of fragmenting the process gases in order to achieve novel surface functionalisation and display a new range of features. Later, people started to look at using vapours from liquids and tried to maximise the retention of functional groups which could be used to subsequently react with other chemicals to obtain a specific chemistry. In order to achieve attachment of long fluorinated chains to the surface, critical for the levels of liquid repellency required, it was necessary to both select a chemical that displayed the necessary functional group, and to apply the right amount of energy; too much would fragment the monomer and too little would not allow polymerisation to occur.

It was discovered that the best way to achieve the power required to initiate the plasma and create reactive intermediates, to allow conventional polymerisation to occur in order to retain the structure as much as possible, is to modulate the power through a pulse cycle. Through careful choice of starting chemical and optimisation of the plasma parameters to maximise the $CF_2:CF_3$ ratio, a pulsed plasma polymerisation process has been developed to provide high levels of both water and oil repellency, achieving repellency to both isopropyl alcohol and heptane on cotton samples. In fact, if very rough materials are used, repellency to hexane can also be achieved. The key is to generate the active species whilst allowing conventional free radical polymerisation to occur.

Results

Synthetic and natural fibres do not show any inherent repellency to oils. Some, particularly the natural fibres, may show a residual degree of hydrophobicity due to the natural oils within the product. However, as the surface tension of the test liquids begins to decrease within the polar series, wetting will soon occur and will usually happen at around 10–20% isopropyl alcohol content (W1–W2).

Several companies report that they can apply oleophobic properties to textiles through post-treatment, either through the use of plasma processing or by a solution-based approach: however, the level of oleophobicity obtained is harder to find. Table 7.4 lists the levels of both water and oil

Table 7.4 List of water and oil repellency values obtained on a variety of textiles. WF and OF represent failure at lowest level

Textile	Untreated		Plasma processed	
	Water	Oil	Water	Oil
100% cotton interlock	W1	OF	W10	O8
65% polyester 35% cotton	WF	OF	W10	O8
65% polyester 35% cotton interlock	W1	OF	W10	O8
Spun viscose woven	WF	OF	W10	O8
50% cotton 50% polyester	WF	OF	W10	O8
Cotton sheeting	WF	OF	W10	O8
100% cotton poplin	WF	OF	W10	O8
Polyester cross tuck	W0	OF	W10	O8
100% Nylon 66 cross-tuck	WF	OF	W10	O8
Wool	W1	OF	W10	O8

repellency obtained using the P2i process on textiles and this can be used as a comparison when other results using different techniques are known. The results illustrate the universal attachment of the chemical groups to a variety of different materials, displaying the highest levels of repellency, all of which were processed in the same chamber run.

Another value that is also reported is the surface energy where two factors are particularly important: (i) the sample should be flat because surface roughness plays a major role in enhancing contact angles and (ii) the test liquids selected need to assess the functionality desired. This latter point means that if one seeks to determine the level of oil repellency, it is necessary that oils are used to test the surface. Methylene iodide has been widely used to calculate the surface energy and determine the degree of oleophobicity; however, it does not resemble oil. Methylene iodide should therefore only be used to benchmark different surfaces reported in the literature and a homologous series of hydrocarbons to probe the level of oleophobicity should be used.

Scale-up challenges

The author's original work in obtaining a high level of both water and oil repellency was carried out in a 470 cm^3 (~0.5 litre) quartz reactor. The next steps were to scale-up the process to provide a cost-effective, value-adding industrial process. The chamber volume was therefore subsequently increased to 3 litres and then 40 litres, both using the same set-up as the original system, with the biggest challenge being how to reduce the pump-down time to an acceptable level. As the amount of textile increases, the amount of water that needs to be removed to reach an adequate base pressure increases and the pumping conductance needs to be taken into consideration.

The first major scale-up step was to a plasma chamber with an internal processing volume of around 300 litres. The major technical differentiators were:

- Stainless steel chamber with internal capacitively coupled electrodes
- Large vacuum pump capacity for evacuating the chamber as quickly as possible
- Alternative monomer inlet system to ensure required processing pressure.

By increasing the conductance of the pipe work between the pump stack and the chamber, shorter pump down times could be ensured. However, with a full loading of textiles, pump-down times could still be lengthy due to removal of water absorbed by hydroscopic materials. What needs to be determined is the base pressure – processing vapour pressure – product out-gassing relationship to ensure that the polymer deposits effectively onto the product without being ‘poisoned’.

Although the increase to 300 litres represents just over a seven-fold scale-up on the previous chamber, using the process to treat textile products is only cost-effective for very high added value items, where performance reigns over cost. A further scale-up was required in order to cope with the demands of the garment and accessories industries, where numerous items could be processed at once. The next processing volume chosen was 2000 litres, to prove that the process could be applied to fully constructed items and treat a wide range of items in sufficient quantities to be able to carry out market trials to benchmark the technology (Figure 7.4).

The chamber has shown many similarities to the 300 litres system and has demonstrated a high degree of homogeneity with regards to the levels of liquid repellency on cellulose substrates and textiles such as polyester.

7.4 P2i’s 2000 litre plasma chamber.

Commercialisation

Processing costs can be competitive, despite the equipment costs. To maximise return on the investment, systems need to operate throughout the day.

When analysing the through-put, there are seven main time-related tasks which cumulatively give the total processing time:

(i) loading of samples
(ii) pumping down to base pressure
(iii) introduction of gases and vapours
(iv) ignition of plasma and processing
(v) turning off plasma power and gases
(vi) evacuating chamber back to base pressure
(vii) venting up to atmosphere and unload.

Tasks (ii) and (iv) are the most time-consuming and need to be reduced as much as possible whilst still achieving the technical requirements. It is quite possible to achieve a total turn-around time of one hour or less.

Durability

Durability often provides an interesting discussion, since all products have different durability requirements. When durability is mentioned, people are often referring to laundry wash durability, dry cleaning or abrasion resistance. However, the number of cycles required varies vastly across the industry. Laundry wash durability is more challenging than durability to dry cleaning cycles, where independent tests on the latter have shown that the pulsed plasma process developed by the author's company could achieve, at its first attempt, the same level of repellency as a leading benchmark for solution-based applications. Further improvements are believed possible once optimised. Mechanical durability has also shown very good comparisons with industry standards where, although some drop off is noticed, very good oil and water repellency is still provided.

7.6 What the future holds

Plasma treatment of textiles for water and oil repellency is both feasible and is currently being used to process a number of products that are either in the later stages of development or already in the market place, proving this is a cost-effective industrial process.

Further optimisation is required to make ever cheaper, automated equipment that will greatly increase the appeal of this technique. In addition, to expand the number of commercial applications, the processing volume of equipment will need to be scaled-up further.

The low-pressure plasma technique for imparting high levels of liquid repellency to textile products has already entered the commercial age due to its added-value performance and its processing and environmental advantages. The next few years will see this become a widely established, cost-effective industrial solution.

7.7 References and sources of further information

Books

- Kissa E (2001), *Fluorinated Surfactants and Repellent,* New York, Marcel Dekker.
- Kissa E (1984) 'Functional finishes' Part B, in Lewin M, Sello, S B (eds), *Handbook of Fibre Science*' Vol. II, New York, Marcel Dekker.
- Grill A (1994), *Cold Plasma Materials Fabrication: From Fundamentals to Applications*, IEEE Press, Piscataway, New Jersey.
- Biederman H (2004), *Plasma Polymer Films*, London, Imperial College Press.

Papers

- Coulson S R, Brewer S A, Willis C R, Badyal J P S (1997), GB Pat. Patent: WO 98/58117.
- Coulson S R, Woodward I S, Badyal J P S, Brewer S A, Willis C R (2000), 'Plasmachemical functionalization of solid surfaces with low surface energy perfluorocarbon chains', *Langmuir*, **16**, 6287–6293.
- Coulson S R, Woodward I S, Badyal J P S, Brewer S A, Willis C R (2000) 'Super-repellent composite fluoropolymer surfaces', *J. Phys. Chem. B*, **104**, 8836–8840.
- Coulson S R, Woodward I S, Badyal J P S, Brewer S A, Willis C R (2000) 'Ultralow surface energy plasma polymer films', *Chem. Mater.*, **104**, 2031–2038.

Other

- 3M water repellency test II, water/alcohol drop test, 3M Test Methods (Oct 1988).
- 3M oil repellency test I, 3M Test Methods (Oct 1988).

8

Interfacial engineering of functional textiles for biomedical applications

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8.1 Introduction

Textiles for clothing increasingly offer special functionalities, such as hydrophobicity, soil release, breathability, UV-stability, flame-protection, antibacterial and antistatic properties. These technical textiles are used, in particular, for outdoor sports, and protective and safety clothing. Other technical textiles include geotextiles, and textiles for architecture, vehicles, transport and packaging. Textiles for medical and healthcare are another well-known industrial sector, with increasing market potential (Rajendran, 2002).

Biomedical textiles must be designed to meet a range of requirements, including minimising non-specific protein adsorption, biocompatibility (blood-, cyto- or tissue-compatibility), and the presence of active functional coatings, such as antibacterial finishes, bioactive layers or drug delivery systems. To achieve these properties, tailor-made surfaces are needed that do not alter the bulk properties of the polymer material used. Sometimes only one type of chemical functionality is required, e.g. carboxyl- or amino-groups homogeneously distributed at a defined density over the total surface area. For some products or production lines, the use of toxic or hazardous chemicals must be avoided. To achieve these requirements, low-pressure plasma functionalisation may be the method of choice.

In this chapter, Section 8.2 gives a brief introduction to technical textiles for biomedical applications and Section 8.3 introduces plasma-based techniques. Different methods for activation, functionalisation, grafting and polymerisation are explained, together with the interaction between plasma and textiles. Specific functionalisation retaining the monomer structure will be examined in detail. In Section 8.4, some technical aspects of experimental set-ups and industrial plants are given, and Section 8.5 deals with assessing the treated samples. Examples of plasma-finished biomedical textiles are given in Section 8.6, and the final section looks at applications and products under investigation or currently on the market, together with an overview of future trends.

8.2 Technical textiles for biomedical applications

Technical textiles are one of the faster-growing sectors of the global textile industry, with the industry moving rapidly toward the manufacture of high added-value textile structures and products, including medical textiles, protective textiles and smart textiles. Textiles used in the medical and applied healthcare and hygiene sectors are an important and expanding part of the industry, and are often referred as to biomedical textiles.

According to Rajendran (2002), four categories of medical textiles can be distinguished:

- non-implantable materials
- implantable materials
- extracorporal devices and
- healthcare and hygiene products.

Medical and healthcare products demonstrate a remarkable range of applications, from simple bandages to biocompatible implants and tissues, antibacterial wound treatment material, prosthetics and intelligent textiles. The different fibres, mono- and multi-filament yarns, woven, knitted, non-woven, and composite fabrics for manufacturing various medical products, are summarised within these four categories in Rajendran (2002).

A biomedical textile is designed according to its final function. The main factors to consider include:

- *Function*: The textile must fulfil the purpose for which it was designed, for example, swabs must be absorbent, sutures may need to be biodegradable, hospital bedding should be comfortable and durable.
- *Cost*: This will depend on the raw materials, manufacturing process and product end-use. Surgeons' gowns and swabs should have a low production cost, while vascular grafts and artificial skin can have a relatively high production cost.
- *Product approval*: Each country has its own regulations and standards for medical textiles. The European Union has introduced Community Legislation to govern medical devices. The three Directives are: Active Implantable Medical Devices, Medical Devices and *In-Vitro* Diagnostic Medical Devices.
- *Biocompatibility*: This refers to possible reactions of the textile with blood and tissue in the body. An implantable device has greater potential for reaction than an external device and is, therefore, subject to tighter regulations. For example, an artificial ligament is permanent and

> internal, so will come into contact with blood cells and the surrounding tissue, whereas an external bandage is temporary and only comes into contact with the outer skin.

The definition of biocompatibility according to the European Society for Biomaterials, is: 'the ability of a material to perform with an appropriate host response in a specific application' (Williams, 1987). It is important to recognise that this definition focuses on a 'specific application'. A specific application imposes requirements on particular properties of the material. This could be bulk properties, such as mechanical strength, or surface properties, such as the surface energy (wettability) or the presence of special functional groups. The second major point in the definition, 'host response', is more complex and embraces the interaction at the interface between biomaterials and tissues, cells (cyto-compatibility), blood (haemo-compatibility) and biological responses such as inflammation, thrombosis and healing (Ratner, 1990). Undesired host reactions are mostly driven by surface/protein interactions. Such protein adsorption occurs on first contact with biological fluids and tissues (Hubbell, 1995a). The nature and amount of the protein adsorption layer depends on the material surface properties, including wettability, polar or ionic interaction, chemical structures and topography of the surface. A good review dealing with the topographical control of cells is given by Curtis (1997). The influence of wettability, hydrophilic or hydrophobic interaction of biomaterials (proteins, cells, etc.) with material surfaces is discussed in detail in an outstanding review by Vogler (1998). Protein adsorption can also be desirable and indeed a prerequisite, for instance for improved cell adhesion and subsequent cell growth as needed, for example, in tissue engineering (Keselowsky, 2005). It is therefore imperative to design and tailor the surface properties of medical textiles according to the intended application.

Tailoring the surface properties of polymer materials such as foils, films, fibres, fabrics, non-wovens, etc. can be achieved by wet chemical treatments or physical techniques such as glow discharge plasma treatment. Systematic investigation of plasma polymerisation started in the 1960s (Goodman, 1960). Plasma-based surface functionalisation is today accepted as an important process for the formation of entirely new materials, and as a valuable technique to functionalise the surfaces of polymers or other materials. Within the last two decades, large improvements have been made in reactor design, the understanding of energy input (continuous wave or pulse techniques), and the polymerisation of monomers while retaining their monomer structure (chemical functionality), making this technique applicable to the development of medical textiles.

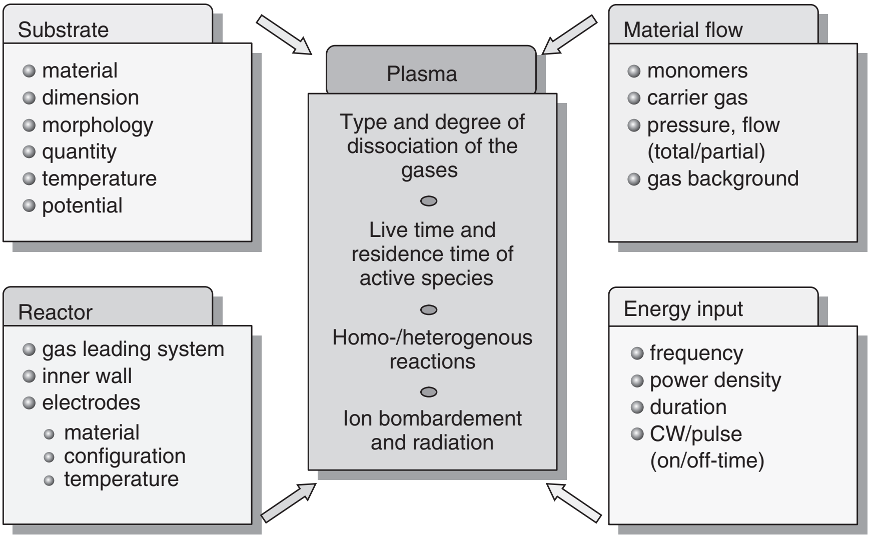
8.3 Plasma treatment for interfacial engineering of technical textiles

The main advantages of plasma treatments are:

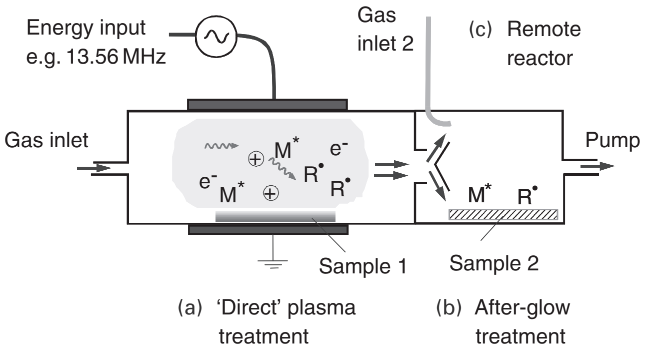
- Modification is limited to the top surface layer and does not affect the bulk properties of the polymer
- Modification by plasma processes is largely independent of the structure or chemical reactivity of the substrate
- A broad range of functional groups can be introduced at the surface, by varying the monomer gas used
- The modification is generally fairly uniform over the whole substrate and
- Plasma treatment is an all-dry process.

The principles of low-pressure cold plasma and atmospheric-pressure cold plasma processes have been described in detail in Chapters 3 and 4, respectively. This chapter provides a brief introduction to low-pressure glow discharge treatment using radio frequency (RF) excited discharges.

The major parameters for this process are shown in Figure 8.1. By varying these parameters, three completely different types of surface modification are possible, etching, functionalisation and coating. Further variations are made possible by altering the treatment conditions of the material itself, such as treating the material directly in the plasma zone, in after-glow or



8.1 Plasma parameters influencing the plasma conditions.



8.2 Schematic view of three different plasma techniques. (a) direct plasma treatment (b) remote technique; the treated samples is positioned outside the direct plasma zone in a second chamber (c) after-glow technique; the polymerisable monomer gas is introduced in the remote zone.

remote plasma, and by using plasma grafting processes (see below). Figure 8.2 gives a schematic view of these process types.

With RF exited discharges, different implementations are possible, such as inductively (ICP) or capacitively coupled plasmas. With ICP, internal or external electrodes can be applied (Hegemann 2005a). Textiles can be treated with or without plasma gas flux through the porous structure of the fabric (Oehr, 1995). To summarise, plasma-based techniques are marked by a great variety of process possibilities, so that processes can be optimised for the desired application of the product. Plasma processes can be developed for almost any surface functionalisation in research laboratories. The challenge is to scale-up laboratory parameters to cope with the typical sizes and speeds needed for industrial operations.

8.3.1 Plasma cleaning/plasma etching/sterilisation

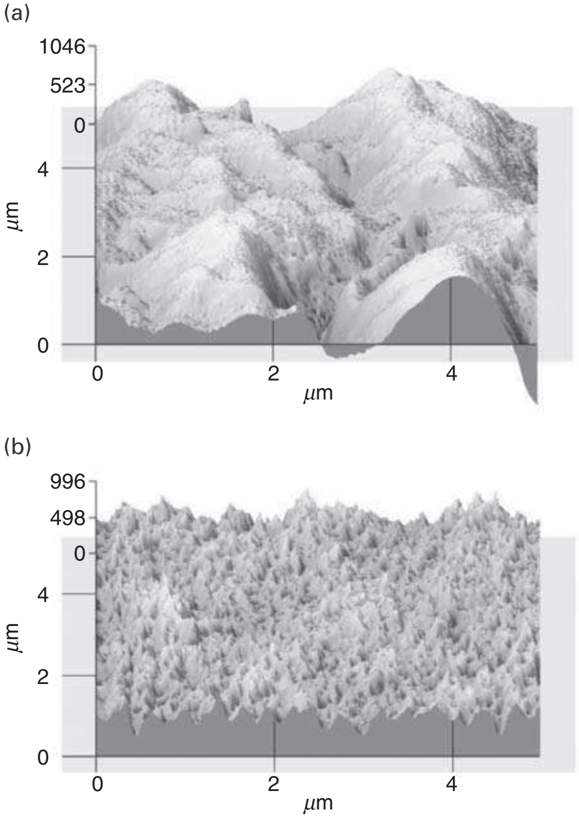
Polymer surfaces can be cleaned or etched, mostly using non-polymerisable gases such as O_2, N_2, H_2, the noble gases or gas mixtures. In the past, plasma etching was mainly used to etch textile fibres to increase tensile strength or resistance to felting shrinkage (Thorsen, 1974; Rakowski, 1989). Etching conditions for plasmas have been used to remove contaminations (lubricants, oils, surfactants, etc.) for decades (Vohrer, 1997). This technique is also important for biomedical applications to some extent, because it can be used to remove thin surface coatings that might otherwise be responsible for inflammatory reactions on contact with cells (Chinn, 1998). Etching has also been shown to promote improved cell attachment in tissue culture studies (Amstein, 1975). Etching is also associated with an increase in wettability (Oehr, 2000).

Sterilisation is a specific method of cleaning. Sterilisation refers to the complete inactivation of all infectious agents. Plasmas have been implicitly assumed to possess sterilisation properties (Boucher, 1985). The mechanisms of plasma sterilisation were analysed in terms of the action of UV emission and interaction with radicals produced in the plasma. A review of the mechanisms of plasma sterilisation can be found in Lerouge (2000). The resulting sterility must be assessed because different micro-organisms and their spores show different mortality rates. *Bacillus subtilis, Bacillus pumilus* or *Bacillus stearothermophilus* spores are commonly used (Vohrer, 1999; Lassen, 2005). Plasma sterilisation is often referred as a low temperature technique, compared to water vapour sterilisation, the former therefore having advantages for the sterilisation of thermo-labile polymers. However, low temperature is not necessarily an accurate description. The sterilisation of, for instance, radiation-stable micro-organisms such as *micrococcus radiodurans*, or high concentrations of spores, can require high energy inputs and long treatment times, which can cause a temperature increase in the substrate up to the melting point of the polymer. This problem was overcome for removing mildew contamination on cellulose fibres (ancient documents) by optimising the process, with an additional increase in paper strength. After-glow hydrogen plasmas are the method of choice (Vohrer, 2001).

Plasma-based etching can change the surface roughness of polymers, and this should be taken into consideration. Figure 8.3 shows AFM pictures of polyethylene before and after oxygen plasma treatment. A dramatic change in the micro-roughness can be seen. Depending on the plasma conditions, similar results can be found on other polymers (see e.g. Wong, 2000). For the textile industry, this effect could be used to generate an anti-pilling finishing, for instance in wool (see Chapter 9). The alteration in surface morphology can also influence blood or cell interaction (see below). The use of non-polymerisable monomer gases not only removes material from the surface and alters its topography, but also leads to a change in chemical composition. For instance, if oxygen is used as the process gas, a great variety of different oxygen-containing functional groups, such as —OH, —C=O, —COOH, will be introduced onto the surface of the material. This is generally referred to as 'unspecific' functionalisation. Nevertheless, this is an important industrial process, used mostly to increase the adhesion properties of materials (Strobel, 1994; Erli, 2003) or the dye-uptake and printability of textiles (Wakida, 1993).

8.3.2 Plasma functionalisation/plasma grafting

The main goal of plasma functionalisation is to create a tailor-made surface with a specific function. Several applications require only one type of



8.3 AFM-picture of polyethylene before (a) and after (b) an oxygen plasma treatment. After the treatment, the micro-roughness of the sample is dramatically changed.

functional group (—COOH, —NH_2, —OH, —CHO, epoxy, etc.) to be added to the material surface, and are typically needed for applications in the medical and pharmaceutical field (Oehr, 2003). The functional groups on the surface serve as anchoring sites for bioactive molecules such as growth factors, biolinkers, peptides and enzymes. Specific plasma functionalisation can be obtained by using monomer gases carrying the desired functional group, mostly combined with a double-bond (—CH═CH—) that easily generates radicals under plasma conditions, or a ring structure that opens during the plasma treatment. Monomers used include acrylic acid (AAc; carboxyl groups, Alexander (1998)), glycidylmethacrylate (GDMA; epoxy groups, Tarducci (2000)), 2-hydroxyethyl methacrylate (HEMA; hydroxy groups, Tarducci (2002)), and diaminocyclohexane (DACH; amino groups, Gölander (1993)).

The main problem when introducing monomers into the plasma zone of the reactor is the fragmentation of the monomer itself. This can be avoided by using mild plasma conditions, such as low plasma power or pulse-plasma techniques. Since the 1990s, pulsed plasmas have been used to retain the chemical structure of the precursors in functionalisation and thin film deposition for medical engineering and for biological applications (Gombotz, 1987; Oehr, 1999). Another technique that retains the monomer structure is usually referred to as plasma grafting. In this method, free radicals are formed on the polymer surface as a result of inert gas plasma treatment. The radicals obtained then react with monomer gases that are introduced consecutively into the treatment chamber. This technique has been used for several decades, see, e.g. Simionescu (1984) and Kato (2003). Teichmann (1975) summarises different activation techniques for grafting onto textile fabrics. Plasma grafting leads to a thin-film coating of the substrates.

Plasma fixation is another method. Here, the textile is covered with a liquid monomer via dip- or spray-coating and the monomer is fixed to the surface by a consecutive plasma process, mostly using inert gas plasmas with argon or helium as the process gas.

8.3.3 Plasma polymerisation/plasma coating

Plasma polymerisation can be defined as ‘the formation of polymeric materials under the influence of plasma’. Solid deposits from organic compounds formed in a plasma, generated by some kind of electrical discharge, were described as early as 1874 (de Wilde, 1874). However, at that time very little was known about polymers, and these deposits were considered to be nothing more than undesirable by-products of the phenomena associated with electrical discharge.

The elemental reactions that occur during plasma polymerisation include fragmentation of monomer molecules, the formation of reactive sites (radicals), and recombination of the activated fragments. The mechanism follows similar steps to traditional radical polymerisation, with the possible inclusion of a re-initiation step. Plasma polymerisation to deposit a thin polymer film on the surface of a material can be done using nearly any organic, organosilicone or organometallic vapour. The substrate material, the application and hence the necessary properties, decide the choice of monomer gas. Treatment time influences the thickness of the applied coatings. There are a number of books dealing with plasma polymerisation; see, for instance, Yasuda (1985), Biederman (1992), and Inagaki (1996).

8.3.4 Plasma functionalisation retaining the monomer structure

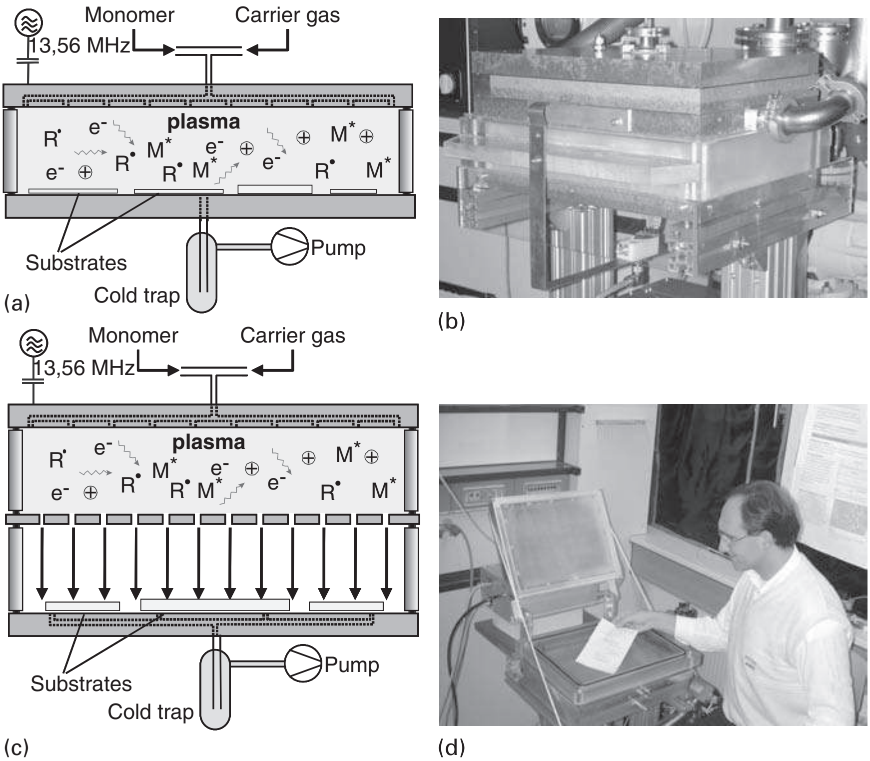
Direct and indirect methods are used to introduce well-defined functionalities using monomers while retaining their structure. In direct methods, the monomer is exposed to very mild plasma environments. For indirect methods, only the substrate is activated and exposed to the monomer after plasma treatment (grafting).

In 1971, Westwood found that plasma polymers possessed a chemically better-defined structure and composition if low power input was used during direct plasma treatment (Westwood, 1971). Pulsed low-power plasma helps avoid excessive monomer fragmentation in the plasma phase and reduces the amount of plasma-induced damage in the polymer. Pulsed plasma polymerisation was introduced first by Tiller (Meisel, 1972), continued by Yasuda (1977), and further developed by a variety of research groups (e.g. Panchalingam, 1993; Kühn, 1999; Oehr, 1999).

To retain the monomer structure during direct plasma processing, the main parameters are low power input (continuous wave or pulse), high working pressure (low mean free path), short treatment time for the molecules in the plasma, minimised ionic bombardment of the surface, and substrate cooling. An early attempt to describe the possibility of structure retention was given by Yasuda, who used an external parameter W/FM to express the plasma energy density, where W is the power input, F the flow rate and M the molecular weight of the monomer (Yasuda, 1978). Smaller so-called Yasuda factors correspond to less fragmentation, so monomers with higher molecular weights in a homologous series are less fragmented than those with lower molecular weights. Unfortunately, with increasing molecular weight, the vapour pressure decreases, and dosage of the monomer becomes much more difficult.

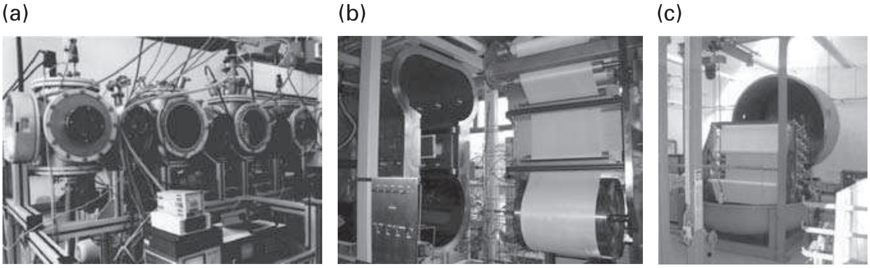
8.4 Plasma reactor techniques

Figure 8.4 gives a schematic view of the DIN-A3-reactor (size $30 \times 40\,\text{cm}^2$; DINA3), designed and developed at the Fraunhofer IGB for the optimisation and development of plasma processes. This laboratory-scale set-up represents a modular concept with symmetrical electrode arrangement and capacitively coupled RF-discharges. This apparatus enables the use of different gas flow regimes within the reactor and for the distance between the electrodes to be varied. The upper version in Figure 8.4 enables gas feeding and pumping on one side, whereas the lower version supports homogeneous ‘flowing through’. A V/I-probe (ENI Model 1065) can be attached to the reactor to measure the applied voltages and current, which, among other things, aids in adjusting the energy input, especially at low power. In such laboratory-scale systems, the best parameter set for a particular process can be determined. For some biomedical applications, this reactor size is sufficient. For textile applications, larger treatment chambers that enable finishing from roll-to-roll are required. Figure 8.5 shows three different sized systems. At Fraunhofer IGB, a strip width of 18 cm can be handled. At



(a) (b) (c) (d)

8.4 Schematic drawings and photographs of the modular, symmetrical reactors for plasma treatment, functionalisation and coating. The upper part represents a design with gas feeding and pumping at one side. The lower part represents a combined reactor with the possibility of direct plasma treatment in the upper chamber and after-glow treatment in the lower chamber.



(a) (b) (c)

8.5 Photos of three plasma roll-to-roll treatment systems. All systems enable a batch treatment. (a) Fraunhofer IGB strip width 18 cm (b) Empa strip width 120 cm (c) FZM Flöha (Niekmi, Russia) strip width 180 cm.

Empa in St Gallen (Hegemann, 2005c) and FZM in Flöha (Poll, 1998; Fuchs, 1999), larger systems are available.

To obtain good penetration of the gas flow into and through the textile structure, Oehr *et al.* (1995) described a system in which the gas flow was forced through the textile. Similar investigations are also found in recent publications (Verschuren, 2005).

8.5 Assessment of the functionalised textiles

The characterisation of plasma-treated textiles is described in detail in Chapter 12. This section is concerned with some general thoughts as well as some specific information regarding the assessment of biomedical textiles.

Polymer materials used in the biomedical sector must satisfy various requirements. To verify these properties, several analytical methods are used before and after chemical and mechanical stressing. Thin plasma polymer coatings have to be stable not only in typical solvents but also, if necessary, in biological liquids such as blood or cell culture medium. It is also extremely important to assess any possible immediate interactions with the respective biological system. The biological response is judged from tests, with cytotoxicity sensitisation, irritation, acute, chronic or subchronic toxicity, gene toxicity, haemocompatibility and carcinogenity being among the most important. The tests applied depend on which type of contact is intended, and the duration of the contact and on the relevant national legislation. The US mandatory FDA norms are generally the determining model.

As mentioned in Section 9.3, plasma treatment can change the morphology (topography) of the polymer material, which may increase the specific surface area. Topography changes are normally investigated using the atomic force microscope (AFM). Any alteration in specific surface area can be analysed from adsorption/desorption isotherms (BET surface area). Changes in the wettability of textile fabrics can be measured via increases in hydrophilicity or hydrophobicity. Hydrophobicity is normally assessed by contact angle measurement, or using well-known textile tests such as the spray test (AATCC 22-1974), Bundesmanntest (DIN 53888) or even the oil repellency test (AATCC 118-1972). To assess hydrophilicity, the captive bubble method is mainly used. Suction tests and capillary rise tests are other methods for assessing the wettability of plasma hydrophilised textile samples (Hossain, 2006; Ferrero, 2003).

As mentioned above, it is important to assess the chemical functionality obtained after treatment. Depending on the film thickness, density and type of chemical functions, several sensitive analytical techniques can be used. Infrared spectroscopy (FTIR), X-ray photoemission spectroscopy (XPS;

ESCA), mass spectroscopy (TOF-SIMS), energy dispersive X-ray analysis (EDX; in combination with scanning electron microscopy, SEM) are some typical techniques.

The lateral distribution of functional groups in surface-treated or modified polymers may also play an important role in determining the interfacial properties of these materials. In biomedical applications, the functional groups must be distributed homogeneously to obtain biocompatible polymeric coatings. Determining spatial distribution and characterising the local environment on a sub-100 nm scale remains extremely difficult, if not impossible, even with the latest analytical techniques.

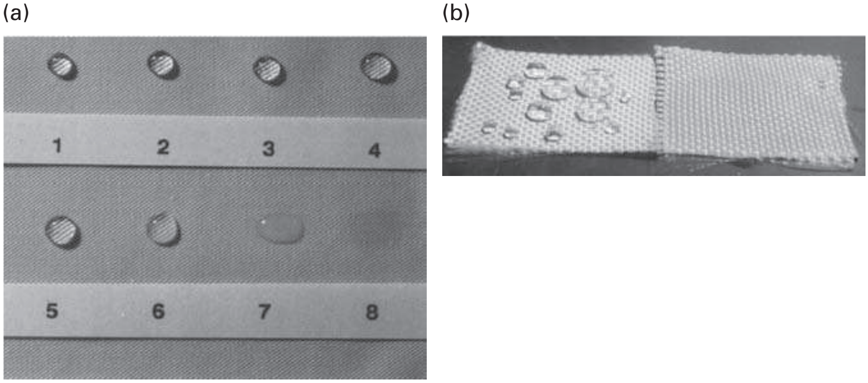
8.6 Surface engineering of biomedical textiles

As mentioned earlier, biomedical textiles are designed according to their function and need for biocompatibility, both of which are dominated by surface properties. Five examples of surface engineering in biomedical textiles are given below.

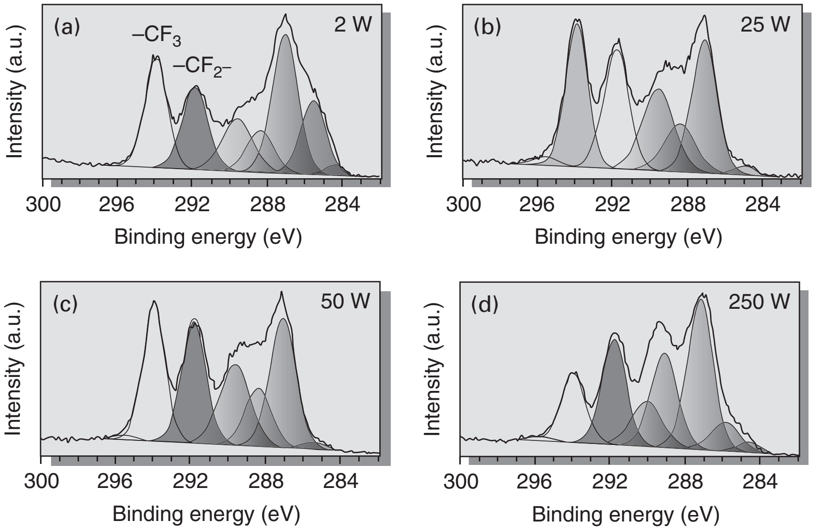
8.6.1 Example 1: Stain-repellent finishing

Hydrophobic and oleophobic stain-repellent textiles are used in leisure suits, safety clothes and surgical gowns, but there is also strong demand from the textile industry for other uses. Although wet chemical hydrophobic treatments such as Scotchguard® finishing are well established, plasma-based treatments are of interest because they use smaller amounts of chemicals and are therefore more environmentally friendly. Plasma grafting and plasma polymerisation have been investigated to assess their suitability for textiles finished with anti-soil, soil-release, and water or oil-repellent finishings. Byrne *et al.* (1972) used acrylic acid, allyl alcohol, vinyl fluoride, 1,1, difluoroethylene and tetrafluoroethylene in RF glow discharges. Millard *et al.* (1972) described a continuous low-temperature discharge treatment to give wool oil repellent properties. Lee *et al.* (1975) used perfluoroacrylates under discharge, after-glow and grafting (after oxygen or hydrogen plasma activation) for oil-repellent finishing in wool.

Fibres that contain water yield an outgassing during low-pressure treatments (Barni, 2003). This water participates in the plasma processes, resulting in the presence of hydrophilic functions on the treated surface. Good hydrophobic or even oleophobic properties can only be achieved by drying the textile prior to plasma finishing (Vohrer, 1998). Figure 8.6a shows an oleophobic finished cotton/polyester fabric with a 7C/8D evaluation, assessed by the 3M oil-repellency test (AATCC 118-1192). Figure 8.6b depicts an aramid fabric after plasma-based hydrophobisation, using



8.6 (a) Cotton/polyester fabric oleophobic finished via plasma-based treatment with perfluoroacrylates. Assessment of the oil repellency in accordance with AATCC 118-1992. (b) Hydrophobic finished aramid fabric. Left side treated, right side untreated.



8.7 C1s-ESCA-Spectras of hydrophobised cotton textiles using different plasma parameters. The increase in —CF_2— groups can be triggered by the adjustment of the plasma conditions.

perfluoropropane as the process monomer. The left side is treated, the right side is untreated.

To optimise the process parameters, assessing the plasma conditions, e.g. via a V/I-probe, optical emission spectroscopy or laser-induced fluorescence, is as important as assessing the treated textile itself. In addition to the textile tests, surface analytical techniques are also needed. Figure 8.7

shows C1s-ESCA-spectras of plasma-hydrophobised textiles under varied plasma parameters. The spectra represents —CF_3 groups at a binding energy of 293.5 eV and —CF_2— groups at a binding energy of 291.5 eV, respectively. Changes in the plasma condition alter the quantitative amount of —CF_3 and —CF_2— groups, which are necessary for the hydrophobic property. Angle resolved ESCA-measurements demonstrate that, after process optimisation, the —CF_3 groups are terminal bonded and consequently located on the outermost surface (Barz, 2005). This is important for a good hydrophobic effect.

Although much research into the plasma-based hydrophobisation of textiles has been carried out (see also Chapter 7), improvements have generally been insufficiently economical to permit commercial adoption, with a few exceptions. This can be traced back to a lack of industrial-sized plants, but mostly to the need for oxygen and water-vapour free atmospheres during the fluorination of the plasma, and the need to clean the treatment chamber regularly. Recent developments emphasise a faster and more controllable hydrophilisation process prior to a common wet-chemical fluorocarbon impregnation. Plasma activation in a low-pressure RF discharge with Ar/O_2 was found to support subsequent wet-chemical impregnation due to enhanced capillary transport (Hegemann, 2005b).

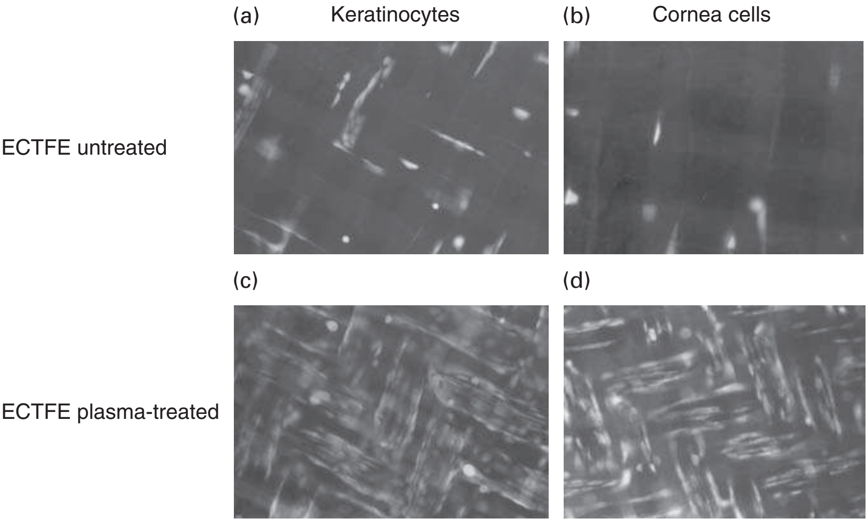
8.6.2 Example 2: Biocompatibility/optimised cell growth

In the early stages of cell attachment, cell–substrate interactions are likely to be a function of the substrate surface chemistry (Wan, 1997), with optimum cell attachment to surfaces with low to moderate levels of hydrophilicity (Lydon, 1985). Cells normally attach to substrates via surface receptors on the cells, which interact with proteins adsorbed onto the surface of the substrate (Hubbell, 1995b). These proteins are adsorbed from either the surrounding serum (culture medium or biological fluid), or secreted by the cells themselves (Saltzman, 1997). Adhesive proteins are said to act as bridging molecules between the cells and the substrate (Lamba, 1998). Due to the hydrophilic and hydrophobic nature of proteins, substrates with an intermediate wettability at the surface usually show maximum cell attachment. Hydrophobic surfaces strongly denature adsorbed proteins (Sigal, 1998).

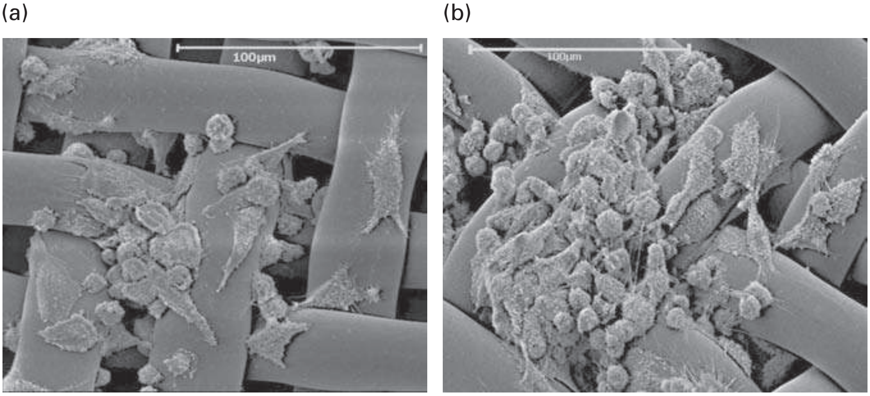
Cells interact with extra-cellular matrix (ECM) proteins. The biological activity of proteins on the surface will depend upon whether specific active peptide sequences in particular proteins are accessible to the arriving cells (Yamada, 1999). Many of the ECM proteins, such as fibronectin, carry a sequence of amino acids to which cells can bind using specific surface receptors called integrins. Integrin-mediated binding of cells is the foundation for cell growth and differentiation, and the dominant mechanism by which cells communicate with non-cellular surroundings (Ruoslahti, 1991). Different functional groups at the substrate surface alter the integrin binding and cell adhesion capability (Keselowsky, 2005), with COOH and OH groups showing greater cell adhesion than CH_3 (Tidwell, 1997). Other substrate properties thought to enhance cell adhesion are positively charged surfaces (Saltzmann, 1997) and grooved surface topographies, which may be due to an increase in surface area (Walboomers, 1999). Polymeric surfaces can undergo conformational rearrangements in response to environmental conditions, and can also exhibit differences in surface roughness and topology depending on process or surface modification (Tyler, 1992). Liu (2005) highlights some of the recent advances in understanding how environmental cues, presented through cellular adhesion, regulate cellular processes such as proliferation and differentiation.

By using glow discharge plasma techniques, the surfaces of different materials can be finished with specific functional groups. The combination of plasma techniques with wet chemistry treatment leads to biomaterials that optimise cell growth. For instance, to enhance corneal epithelial cell attachment and growth, an ammonia plasma treatment has been applied to artificial corneas fabricated from poly (hydroxyethyl methacrylate) (Sipehia, 1993).

Figure 8.8 shows the growth of ceratinocytes and cornea cells on a technical textile (ECTFE) before and after oxygen plasma treatment. Before the plasma treatment, only a few cells attach and are cultured on the textile. The increase in cell growth can be linked to an increase in wettability and



8.8 Growth of ceratinocytes and cornea cells on a technical textile before and after a plasma treatment.



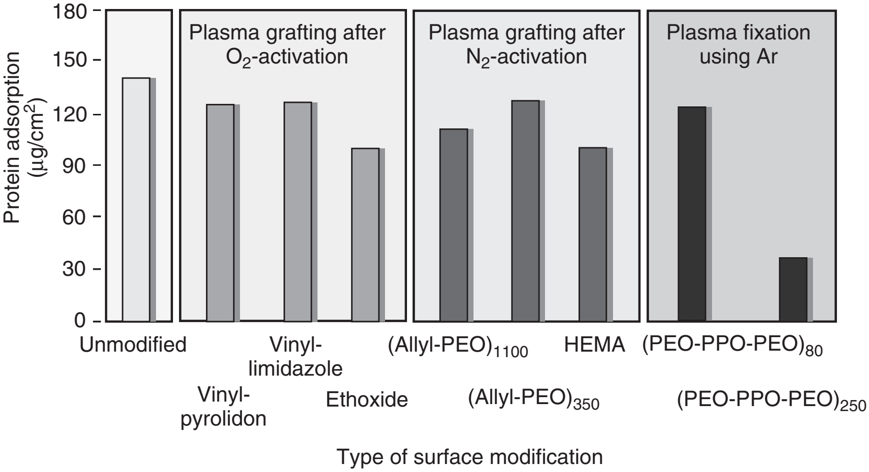
8.9 SEM pictures of stem cells attached onto a polyester fabric after plasma.

the introduction of oxygen-containing functional groups. The attachment of cells is the first step for cell culturing on substrates. Figure 8.9 shows scanning electron microscopy images of stem cells attached onto a plasma-modified polyester fabric.

8.6.3 Example 3: Biocompatibility/unspecific protein adsorption/biofouling

As mentioned in Example 2, contact of synthetic materials with biological fluids leads instantly to an unspecific adsorption of proteins onto the material surface. In most applications, this is undesirable because bacteria cells will also adhere to the material surface due to proteins in their extracellular matrix. Bacterial adhesion is often referred to as 'biofouling'. Plaque on teeth or blocking of catheters can result from this effect. A concise review of the mechanisms of bacterial adhesion to biomaterial surfaces is given in Dankert (1986) and An (1998).

Polyethylene glycol (PEG) is an amphoteric material that decreases the adsorption of proteins and the adhesion of cells. PEG is used as the benchmark for comparing new antifouling materials (Dalsin, 2005; Harris, 1992). PEGylated surfaces are of interest in biomedical applications. The simplest surface modification technique, direct adsorption of PEG, leads to only weak bonding behaviour. Gombotz *et al.* (1991) used allylamine plasma glow discharge to introduce amine groups onto the surface of poly(ethylene terephthalate), which were subsequently reacted with amine-terminated PEO using cyanuric chloride chemistry. A significant reduction in the adsorption of albumin and fibrinogen was achieved, despite an incomplete surface coverage. Ratner and coworkers (Mar, 1999; Shen, 2003) have



8.10 Minimisation of unspecific protein adsorption (IgG) through different surface modifications. The measurements were carried out after a stability test using 1 M NaOH for 1 h at 50 °C.

demonstrated that PEG-like surfaces, which resist protein adsorption and cell adhesion, can be formed using plasma deposition of short-chained oligomers.

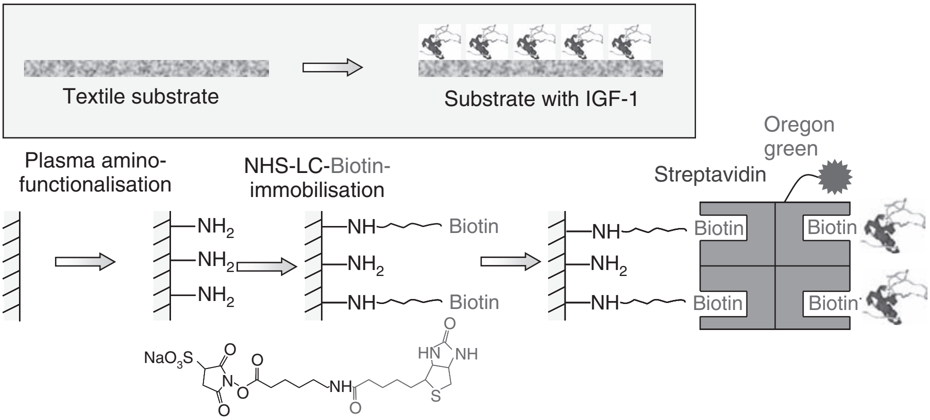
Figure 8.10 shows the results of minimising unspecific protein adsorption (IgG) using different surface modifications. The measurements were carried out after a stability test using 1 M NaOH for 1 h at 50°C, and different plasma-based techniques were investigated. Grafting after activation with oxygen or nitrogen plasmas and plasma fixation experiments were carried out. The best results were obtained with $(PEO\text{-}PPO\text{-}PEO)_{250}$ fixed after a dip coating and with a consecutive plasma treatment.

8.6.4 Example 4: Biocompatibility/immobilisation of ligand–receptor systems

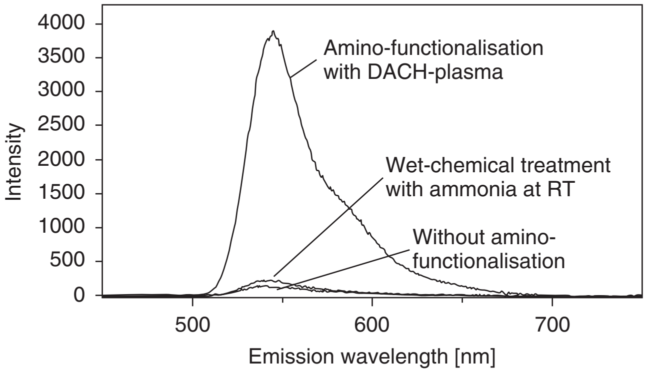
Numerous biological compounds have properties of specific recognition, often referred as to ‘affinity’. Enzymatic reactions, for example, are controlled by the affinity between an enzyme and its substrate. This type of specific interaction can be used for the development of biosensors or for the specific bonding of biomolecules.

Polypeptide growth factors are powerful regulators of a variety of cellular behaviours, including cell proliferation, migration, differentiation and protein expression, and these molecules are being developed as important therapeutics in tissue regeneration, e.g. in closing bone defects and in healing chronic ulcers in the skin. The ability of immobilised growth factors to remain biologically active has been demonstrated in the very well-characterised system of epidermal growth factor conjugated to synthetic polymer surfaces, where it was shown to be capable of directing hepatocytes to maintain their liver-specific morphology and function (Kuhl, 1996).

In collaboration with the German competence centre for biomaterials and artificial organs (BMOZ), a wound-healing non-woven pad was investigated using immobilised growth factor IGF-1, known for its support in wound healing (Ulcera). Non-wovens made of polyurethane and other substrates were used. To immobilise the growth factor, the bio-linker system biotin/streptavidin was chosen. A prerequisite for attaching biotin onto a substrate surface is the presence of free primary amino groups. Amino groups can be generated at material surfaces via plasma treatment with ammonia as the process gas. A more defined functionalisation can be obtained using allyl amine or diaminocyclohexane (DACH) with optimised plasma conditions (Müller, 1999). Figure 8.11 shows the outline of the functionalisation steps needed to immobilise the growth factor onto the non-woven material. Step 1 represents the specific functionalisation of the substrate material via plasma treatment with diaminocyclohexane as the monomer gas. The amino groups serve as anchor sites for the reaction with biotin, carried out in a wet chemical treatment step. To obtain a complete mono-molecular covering with biotin, at least two molecules should be immobilised per square nanometre. On this mono-functionalised surface, fluorescence-labelled streptavidin can be bonded onto the biotin to obtain a spacer for the biotinylated IGF-1. Figure 8.12 shows the fluorescence intensities of an untreated polyurethane non-woven compared with a



8.11 Specific bio-functionalisation. After amino functionalisation of the polyurethane non-woven via DACH-plasma treatment, NHS-LC-Biotin and consequently streptavidin were fixed onto the surface. This surface can be treated with biotinylated growth factors (e.g. IGF-1) to immobilise the bioactive species.



8.12 Fluorescence intensities measured on polyurethane non-woven after immobilisation of the fluorescence-labelled biotin/streptavidin biolinker system. An untreated non-woven is compared with amino-functionalised samples using wet-chemical treatment with ammonia at room temperature and plasma-based treatment with DACH as monomer, respectively.

wet-chemical treatment with ammonia at room temperature and a plasma-functionalised sample. The plasma treatment provides the highest amount of free amino consecutively linked with the fluorescence-labelled biolinker system. The success of the last step, the immobilisation of the growth factor, was checked with an ELISA test (enzyme-linked immunosorbent assay) (Beeh, 2000).

8.6.5 Example 5: Biocompatibility/antibacterial properties

The use of antimicrobial agents for preserving fibres and preventing the transmission of disease by materials dates back to ancient times. Linen cloth containing salt as a preservative was used by the Egyptians to wrap mummies. Ancient literature is replete with the use of silver, sulfur and other germicidal agents on clothing for health purposes. A historical review is given in Vigo (1993).

Microbial attack on textiles can be classified into two main categories. Firstly, those that are detrimental to the consumer, such as odour formation and contamination, and secondly, those that affect the fabric itself, in terms of strength reduction and quality loss. Antimicrobials are defined as agents that either kill micro-organisms (biocidal) or that inhibit their growth (biostatic). The mechanisms by which they act include:

- cell wall damage
- alteration of cell wall permeability
- inhibition of cell wall synthesis
- inhibition of protein and nucleic acid synthesis

- inhibition of enzyme action and
- inactivation of DNA.

An antimicrobial textile can act in two distinct ways – by contact and by diffusion. In the contact method, the antimicrobial agent is placed on the fibre and does not disperse, so it acts only when micro-organisms touch the fibre. In the diffusion method, the antimicrobial agent is placed on the surface or in the fibre and then migrates more or less rapidly in a humid external medium to reach the micro-organisms and inhibit their growth.

Various different agents are used to give textiles antimicrobial properties, including metals and metal salts, mostly based on silver or copper (Nakashima, 2001; Klueh, 2000); quarternary ammonium salts (Diz, 2001; Kim, 2001); N-halamines, which also enable a regeneratable finish (Eknoian, 1998); Sun, 1998); organic molecules (e.g. triclosan (Bhargava, 1996); and natural substances (e.g. chitosan (Shin, 1999) or lysozyme (Edwards, 2000)). Antibiotics may also be necessary, but, due to the possible formation of resistant strains, antibiotics should be used only for medical indications.

Fabrication methods for antimicrobial textiles can be classified into two categories, the addition of an antimicrobial agent to the polymer before extrusion (intrinsically antimicrobial fibres), or post-treatment of the fibre or fabric during the finishing stages. Plasma-based treatments can be used to create antimicrobial coatings on textiles. Chitosan can be grafted onto plasma-functionalised polymer surfaces if carboxyl groups are generated. Hun *et al.* (2001) describe the activation of PET with an oxygen plasma glow discharge treatment followed by wet chemical acrylic acid grafting and a subsequent reaction with chitosan. The poly(acrylic acid) can also be plasma polymerised on nearly all substrates using low power or pulsed plasmas (Sciarratta, 2003). A subsequent wet chemical treatment with silver nitrate produces silver carboxylated coatings, resulting in an antimicrobial finish due to the release of Ag^+ ions (Sciarratta, 2002). The silver carboxylate can also be reduced at suitable pH with mild reducing agents to obtain silver clusters at the fabric surface (Yuranova, 2003). The deposition of metallic silver can be also carried out using the magnetron sputter technique. To achieve a good adhesion of silver, low frequency (50 Hz) (Scholz, 2005) or RF (13.56 MHz) (Hegemann, 2004) plasma treatment with air or O_2/Ar-mixtures should be applied prior to magnetron sputtering.

8.7 Outlook

Plasma-based treatments are ideal for the modification of textiles due to the great variety of process types and process parameters. In the laboratory, almost all types of functionalisation of textiles can be obtained, including flame retardancy (Tsafack, 2004) antistatic finishing and self-cleaning

(Bozzi, 2005), and antibacterial finishing (Szymanowski, 2005) by applying TiO_2-layers via a plasma-enhanced CVD process. For industrial applications, improvements in machinery over the last few decades mean that several companies can now offer large-scale systems. Nevertheless, the systems are mainly used to increase hydrophilicity (for wettability, dye-uptake and printability), because this process is easier to handle and air can be used as the process gas. For hydrophilisation, atmospheric-pressure plasma treatment is the method of choice because the finishing can be done roll-to-roll. For special coatings that require plasma polymerisation, commercial applications are still unavailable, due to the more complicated process, longer process times and higher production costs. Another problem is the fact that plasma polymerisation also coats the electrodes and the inner walls of the system components, so the equipment must be cleaned regularly to avoid alterations in the plasma parameters and therefore a change in the properties. But new demands for technical textiles will drive continuing developments in plasma-based techniques due to the outstanding possibilities for finishing material surfaces without alteration of their bulk properties. Plasma-based treatments of fibres and yarns, important to avoid the shadowing effects which can occur during fabric treatment, will be improved to overcome slow treatment speeds and make them available for commercial applications.

8.8 References

Alexander M R, Duc T M (1998), 'The chemistry of deposits formed from acrylic acid plasmas', *J Mater Chem*, **8**(4) 937–943.

Amstein C F, Hartmann P A (1975), 'Adaption of plastic surface for tissue culture by glow discharge', *J Clinic Microbiol*, 46–54.

An Y H, Friedmann R J (1998), 'Concise review of mechanisms of bacterial adhesion to biomaterial surfaces', *J Biomed Mater Res (Appl Biomater)*, **43**, 338–348.

Barni R, Riccardi C, Fontanesi M (2003), 'Experimental study of outgassing from textile materials', *J Vac Sci Technol*, **A21**, 683–689.

Barz J, Haupt M, Vohrer U, Hilgers H, Oehr C (2005), 'Ultra-thin carbon–fluorine film processing', *Surf Coat Technol*, **200**, 453–457.

Beeh M (2000), *Immobilisierung des Wachstumsfaktors IGF-1 an aminofunktionalisierten PUR-Vliesen für den Einsatz in der Wundheilung*, Diploma-Thesis, Universität Stuttgart.

Bhargava H N, Leonard P A (1996), 'Triclosan: applications and safety', *Am J Infect Control*, **24**, 209–218.

Biederman H, Osada Y (1992), '*Plasma Polymerization Processes', Plasma Technology 3*, Elsevier Science Publishers B.V., Amsterdam.

Boucher R M G (1985), 'State of the art in gas plasma sterilization', *Med Dev Diagn Ind*, **7**, 241–245.

Bozzi A, Yuranova T, Guasaquillo I, Laub D, Kiwi J (2005), 'Self-cleaning of modified cotton textiles by TiO_2 at low temperature under daylight irradiation', *J Photochemistry Photobiology A: Chemistry*, **174**, 156–164.

Byrne G A, Brown K C (1972), 'Modification of textiles by glow-discharge reactions', *J Soc Dyers and Colourists*, **88**(3), 113–117.

Chinn J A, Sauter J A, Phillips R E Jr, Kao W J, Anderson J M, Hanson S R, Ashton T R (1998), 'Blood and tissue compatibility of modified polyester: thrombosis, inflammation, and healing', *J Biomed Mater Res*, **29**(1), 130–140.

Curtis A, Wilkinson C (1997), 'Topographical control of cells', *Biomaterials*, **18**, 1573–1583.

Dalsin J L, Messersmith P B (2005), 'Bioinspired antifouling polymers', *Materials Today*, **8**(9), 38–46.

Dankert J, Hogt A H, Feijen J (1986), 'Biomedical polymers: bacterial adhesion, colonization, and infection', *CRC Crit Rev Biocompat*, **2**, 219–301.

de Wilde P (1874), 'Vermischte Mittheilungen', *Ber Dtsch Chem Ges*, **7**, 352–357.

Diz M, Infante M R, Erra P (2001), 'Antimicrobial activity of wool treated with a new thiol cationic surfactant', *Textile Res J*, **71**(8), 695–700.

Edwards J V, Sethumandhavan K, Ullah A H J (2000), 'Conjugation and modelled structure/function analysis of lysozyme and glycine esterified cotton celullose fibres', *Bioconjugate Chem*, **11**, 469–473.

Eknoian M W, Worley S D (1998), 'New N-halamine biocidal polymers', *J Bioactive and Compatible Polymers*, **13**, 303–314.

Erli H J, Marx R, Paar O, Niethard F U, Weber M, Wirtz D C (2003), 'Surface pretreatments for medical application of adhesion', *Biomedical Engineering Online*, **2**, 15; http://www.biomedical-engineering-online.com/content/2/1/15.

Ferrero F (2003), 'Wettability measurements on plasma treated synthetic fabrics by capillary rise method', *Polym Testing*, **22**, 571–578.

Fuchs H, Bochmann R, Poll H-U, Schreiter S (1999), 'Plasmabehandlung cellulosischer Fasermaterialien', *Textilveredelung*, 3/4, 23–28.

Gölander C-G, Rutland M W, Cho D L, Johansson A, Ringblom H, Jönsson S, Yasuda H K (1993), 'Structure and properties of diaminocyclohexane plasma polymer films', *J Appl Polym Sci*, **49**, 39–51.

Gombotz W R, Hoffmann A S (1987), 'Gas discharge technique for biomaterial modification', *CRC Crit Rev Biocompat*, **4**(1), 1–42.

Gombotz W R, Wang G H, Horbett T A, Hoffman A S (1991), 'Protein adsorption to poly(ethylene oxide) surfaces', *J Biomed Mater Res*, **25**(12), 1547–1562.

Goodman J (1960), 'The formation of thin polymer films in the gas discharge', *J Polym Sci*, **144**, 551–552.

Harris J M (Ed.) (1992), *Poly(Ethylene Glycol) Chemistry: Biotechnical and Biomedical Application*, New York, Plenum Press.

Hegemann D, Fischer A (2004), 'Plasmafunktionalisierung von Textilien und Fasern', *Vakuum in Forschung und Praxis*, **16**(5), 240–244.

Hegemann D, Oehr C, Fischer A (2005a), 'Design of functional coatings', *J Vac Sci Technol*, **A 23**(1), 5–11.

Hegemann D (2005b), 'Stain-repellent finishing on fabrics' *Adv Eng Mater*, **7**(5) 401–404.

Hegemann D, Hossain M M (2005c), 'Influence of non-polymerizable gases added during plasma polymerization', *Plasma Process Polym*, **2**, 554–562.

Hossain M M, Hegemann D, Hermann A S (2006), 'Contact angle determination on plasma-treated poly(ethylene terephthalate) fabrics and foils, *J Appl Polym Sci* (to be published).

Hubbell J A, Langer R (1995a), 'Tissue engineering', *Chem Eng News*, **73**, 42–54.

Hubbell J A (1995b), 'Biomaterials in tissue engineering', *Bio/Technology*, **13**, 565–576.

Hun M W, Kang I-K, Lee D H *et al.* (2001), 'Surface characterization and antibacterial activity of chitosan-grafted poly(ethylene terephthalate) prepared by plasma glow discharge', *J Appl Poly Sci*, **81**, 2769–2778.

Inagaki N, (Ed.) (1996), *Plasma Surface Modification and Plasma Polymerization*, Technomic Publishing Inc., USA.

Kato K, Uchida E, Kang E T, Uyama Y, Ikada Y (2003), 'Polymer surface with graft chains', *Prog Polym Sci*, **28**, 209–259.

Keselowsky B G, Collard D M, Garcia A J (2005), 'Integrin binding specifity regulates biomaterial surface chemistry effects on cell differentiation', *PNAS*, **102**(17), 5953–5957.

Kim Y E, Sun G (2001), 'Durable antimicrobial finishing of nylon fabrics with acid dyes and a quarternary ammonium salt', *Textile Res J*, **71**(4), 318–323.

Klueh U, Wagner V, Kelly S, Johnson A, Bryers J D (2000), 'Efficacy of silver-coated fabric to prevent bacterial colonization and subsequent device-based biofilm formation', *Mater Res (Appl Biomater)*, **53**, 621–631.

Kuhl P R, Griffith-Cima L G (1996), 'Tethered epidermal growth factor as a paradigm for growth factor-induced stimulation from the solid phase', *Nat Med*, **2**, 1022–1027.

Kühn G, Weidner St, Decker R, Ghode A, Friedrich J (1999), 'Selective surface functionalization of polyolefins by plasma treatment followed by chemical reduction', *Surf Coat Technol*, 116–119, 796–801.

Lamba N *et al.* (1998), 'Cell–synthetic surface interactions', in Patrick *et al.*, *Frontiers In Tissue Engineering*, Pergamon, 121–132.

Lassen K S, Johansen J E, Grün R (2005), 'Comparison of two radio-frequency plasma sterilization processes using microspot evaluation of microbial inactivation', *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, DOI 10.1002/jbm.b.3047.

Lee K S, Pavlath A E (1975), 'The effect of afterglow, ultaviolet radiation and heat on wool in an electrical glow discharge', *Textile Res J*, **45**, 625–629.

Lerouge S, Fozza A C, Wertheimer M R, Marchand R, Yahia L H (2000), 'Sterilization by low-pressure plasma: the role of vacuum-ultraviolet radiation. Plasmas and polymers', *Plasma Polym*, **5**(1), 31–46.

Liu W F, Chen C S (2005), 'Engineering biomaterials to control cell function', *Materialstoday*, **8**(12), 28–35.

Lydon M, Minett T W, Tighe B J (1985), 'Cellular interactions with synthetic polymer surfaces in culture', *Biomaterials*, **6**, 396–402.

Mar M N, Ratner B D, Yee S S (1999), 'An intrinsically protein-resistant surface plasmon resonance biosensor based upon a RF-plasma-deposited thin film', *Sensors and Actuators*, **B 54**, 125–131.

Meisel J, Tiller H-J (1972), 'Untersuchungen zur Herstelung von Glimmpolymeren niedrigen Molekulargewichtes', *Z Chem*, **7**, 275–276.

Millard M M, Lee K S, Pavlath A E (1972), ‘Continuous low-temperature discharge treatment of wool yarn; a process for making wool yarn oil repellent and shrink resistant’, *Textile Res J*, **42**, 307–313.

Müller M, Oehr C (1999), ‘Plasma aminofunctionalisation of PVDF microfiltration membranes’, *Surf Coat Technol*, 116–119, 802–807.

Nakashima T, Sakagami Y, Itoi H, Matsuo M (2001), ‘Antibacterial activity of cellulose fabrics modified with metallic salts’, *Textile Res J*, **71**(8), 688–694.

Oehr C, Schindler B, Vohrer U, Müller M (1995), ‘Verfahren und Vorrichtung zur Plasmamodifizierung von flächigen porösen Gegenständen’, Patent DE 44 32 919 C2.

Oehr C, Müller M, Elkin E, Hegemann D, Vohrer U (1999), ‘Plasma grafting – a method to obtain monofunctional surfaces’, *Surf Coat Technol*, 116–119, 25–35.

Oehr C, Janocha B, Hegemann D, Vohrer U, Brunner H (2000), ‘Plasmabehandlung von Polymeren für biologische und medizinische Anwendungen’, *Vakuum in Forschung und Praxis*, **5**, 313–317.

Oehr C (2003), ‘Plasma surface modification of polymers for biomedical use’, *Nucl Instr Methods in Phys Research*, **B 208**, 40–47.

Panchalingam V, Poon B, Huo H-H, Savage C R, Timmons R B, Eberhardt R C (1993), ‘Molecular surface tailoring of biomaterials via pulsed RF plasma discharges’, *J Biomater Sci Polym*, **5**(1/2), 131–145.

Poll H-U, Schreiter S (1998), ‘Industrienahe Plasmabehandlung textiler Bahnware’, *Melliand Textilberichte*, **6**, 466–468.

Rajendran S, Anand S C (2002), ‘Development in medical textiles’, *Textile Progress*, 10–13.

Rakowski W (1989), ‘Plasma modification of wool under industrial conditions’, *Melliand Textilberichte*, **70**, 780–785.

Ratner B D, Chilkoti A, Lopez G P (1990), ‘Plasma deposition and treatment for biomaterial applications, in d’Agostino R (editor), *Plasma Deposition, Treatment and Etching of Polymers*, San Diego: Academic Press p 463–516.

Ruoslahti E (1991), ‘Integrins’, *J Clin Invest*, **87**, 1–5.

Saltzman W (1997), ‘Cell interactions with polymers’, in Lanza R, Langer R, Chick W, *Principles In Tissue Engineering*, RG Landes Company, 225–236.

Scholz J, Nocke G, Hollstein F, Weissbach A (2005), ‘Investigations on fabrics coated with precious metals using magnetron sputter technique with regard to their anti-microbial properties’, *Surf Coat Technol*, **192**, 252–256.

Sciarratta V, Trick I, Vohrer U, Oehr (2002), *Fraunhofer IGB internal report*.

Sciarratta V, Vohrer U, Hegemann D, Müller M, Oehr C (2003), ‘Plasma functionalization of polypropylene with acrylic acid’, *Surf Coat Technol*, 174–175, 805–810.

Shen M, Wagner M S, Castner D G, Ratner B D, Horbett T A (2003), ‘Multivariate surface analysis of plasma-deposited tetraglyme for reduction of protein adsorption and monocyte adhesion’, *Langmuir*, **19**(5), 1692–1699.

Shin Y, Yoo D I, M K (1999), ‘Antimicrobial finishing of polypropylene nonwoven fabric by treatment with chitosan oligomer’, *J Appl Polym Sci*, **74**, 2911–2916.

Sigal G B, Mrksich M, Whitesides G M (1998), ‘Effect of surface wettability on the adsorption of proteins and detergents’, *J Am Chem Soc*, **120**, 3464–3473.

Simionescu C I, Denes F, Macoveanu M M, Negulescu I (1984), 'Surface modification and grafting of natural and synthetic fibers and fabrics under cold plasma conditions', *Makromol Chem Suppl*, 8, 17.

Sipehia R (1993), 'X-ray photoelectron spectroscopy studies, surface tension measurements, immobilization of human serum albumin, human fibrinogen and human fibronectin onto ammonia plasma treated surfaces of biomaterials useful for cardiovascular implants and artificial cornea implants,' *Biomat Art Cells & Biotech*, **21**, 647–658.

Strobel M, Lyons C S, Mittal K L (Eds.) (1994), *Plasma Surface Modification of Polymers: Related to Adhesion*, Utrecht, VSP BV.

Sun G, Xu X (1998), 'Durable and regenerable antibacterial finishing of fabrics: biocidal properties', *Textile Chemist and Colorist*, **30**(6), 26–30.

Szymanowski H, Sobczyk A, Gazicki-Lipmann M, Jakubowski W, Klimek L (2005), 'Plasma enhanced CVD deposition of titanium oxide for biomedical application', *Surf Coat Technol*, **200**, 1036–1040.

Tarducci C, Kinmond E J, Badyal J P S, Brewer S A, Willis C (2000), 'Epoxide-functionalized solid surfaces', *Chem Mater*, **12**, 1884–1889.

Tarducci C, Schofield W C E, Badyal J P S, Brewer S A, Willis C (2002), 'Monomolecular functionalization of pulsed plasma deposited poly(2-hydroxyethyl methacrylate) surfaces', *Chem Mater*, **14**(6), 2541–2545.

Teichmann R (1975), 'Durch Pfropfpolymerisation realisierbare Eigenschaftsverbesserungen an textilen Substraten – Eine Literaturübersicht', *Faserforschung und Textiltechnik*, **26**(2), 66–88.

Thorsen W J (1974), "Modification of the cuticle and primary wall of cotton by corona treatment', *Textile Research Journal*, **44**, 422–428.

Tidwell C D, Ertel S I, Ratner B D (1997), 'Endothelial cell growth and protein adsorption and terminally functionalized, self-assembled monolayers of alkanethiolates on gold', *Langmvir*, **13**, 3404–3413.

Tsafack M-J, Hochart F, Levalois-Grützmacher J (2004), 'Polymerization and surface modification by low pressure plasma technique', *Eur Phys Appl Phys*, **26**, 215–219.

Tyler B J, Ratner B D, Castner D G, Briggs D (1992), 'Variation between biomer lots. I. Significant differences in the surface chemistry of two lots of commercial poly(ether urethane)', *J Biomed Mater Res*, **26**, 273–289.

Verschuren J, Kiekens P (2005), 'Gas flow around and through textile structures during plasma treatment', *AUTEX Research J*, **5**(3), 154–161.

Vigo T L (1993), 'Antimicrobial fibres and polymers' in Seymour R B, Porter R S (Eds), *Manmade Fibers: Their Origin and Development*, London, Elsevier Applied Science, p, 214–226.

Vogler E A (1998), 'Structure and reactivity of water at biomaterial surfaces', *Adv Colloid Interface Sci*, **74**, 69–117.

Vohrer U (1997), 'Fragen und Antworten zur Plasmafeinreinigung', *Galvanotechnik*, **88**(4), 1256–1263.

Vohrer U, Müller M, Oehr C (1998), 'Glow-discharge treatment for the modification of textiles', *Surf Coat Technol*, **98**, 1128–1131.

Vohrer U, Trick I, Oehr C (1999), 'Development of a new sterilization process using plasma technology', *Pharma International*, **2**, 110–111.

Vohrer U, Trick I, Bernhardt J, Oehr C, Brunner H (2001), 'Plasma treatment – an increasing technology for paper restoration?', *Surf Coat Technol*, 142–144, 1069–1073.

Wakida T, Tokino S, Niu S, Lee M, Uchiyama H, Kaneko M (1993), 'Dying properties of wool treated with low-temperature plasma under atmospheric pressure', *Textile Res J*, **63**(8), 438–442.

Walboomers, X F, Monaghan W, Curtis A S, Jansen J A (1999), 'Attachment of fibroblasts on smooth and microgrooved polystyrene', *J Biomed Mater Res*, **46**, 212–220.

Wan H, Williams R L, Doherty P J, Williams D F (1997), 'A study of cell behaviour on the surfaces of multifilament materials', *Journal of Materials Science: Materials In Medicine*, **8**, 45–51.

Westwood A R (1971), *Eur Polym J*, **7**, 363–375.

Williams D F (1987) (Ed.), 'Definitions in biomaterials', *Progress in Biomedical Engineering*, 4, Amsterdam, Elsevier Press.

Wong K K, Tao X M, Yuen C W M, Yeung K W (2000), 'Topographical study of low temperature plasma treated flax fibers', *Textile Res J*, **70**(10), 886–893.

Yamada K (1999), 'Adhesive recognition sequences' *J Biol Chem*, **266**, 12809–12812.

Yasuda H (1985) (Ed.), *Plasma Polymerization*, Academic Press Inc., London.

Yasuda H, Hsu T (1977), 'Some aspects of plasma polymerization investigated by pulsed RF discharge', *J Appl Polym Sci*, **15**(1), 81–97.

Yasuda H, Hirotsu T (1978), 'Critical evaluation of conditions of plasma polymerization', *J Polym Sci Polym Chem Ed*, **16**, 743–759.

Yuranova T, Rincon A G, Bozzi A, Parra S, Pulgarin C, Albers P, Kiw J (2003), 'Antibacterial textiles prepared by RF-plasma and vacuum-UV mediated deposition of silver', *J Photochem Photobiol A: Chemistry*, **161**, 27–34.

9

Plasma modification of wool

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9.1 Introduction

Though one of the oldest raw materials for clothing, wool cannot be regarded as an old fashioned textile fibre. Wool still represents one of the most fascinating materials, a masterpiece of design which could never be duplicated in a factory. This is due to a highly complex chemical and physical structure which is responsible for superior natural fibre properties.

The wool fibre exhibits a typical core–shell structure consisting of an inner protein core, the cortex, which is covered by overlapping cuticle cells with scale edges pointing in the direction of the fibre. The cortex is built up of spindle-shaped interdigitated cells, consisting mainly of *ortho* and denser *para* cells, which divide the stem of a fine fibre into two halves. This bilateral asymmetry results in a natural crimp of the fibre being jointly responsible for crease resistance and, due to permitting enmeshed air, for insulation against loss of heat or protection from heat. The cortex contains macrofibrils formed by fibril-structured α-helical keratin proteins embedded in a cystine-rich protein matrix. Whereas the α-helical material is responsible for the fibre resilience, a diamino acid, cystine, cross-links the protein chains and thus stabilises the wool fibre towards environmental influences. Cystine is also responsible for the high wet strength, moderate swelling and insolubility of the fibre. Wool is hygroscopic and the amount of water taken up corresponds to the relative humidity and temperature of the surrounding air. However, only the interior of the wool fibre is able to absorb water vapour to an extent of up to 30% o.w.f., whereas the fibre surface is water repellent due to the hydrophobicity of the outer surface of the cuticle. This apparently contradictory behaviour results in an intelligent moisture management system being responsible for the well-known wearing comfort of wool.

The hydrophobic nature of the wool fibre is caused by covalently bound, branched fatty acids, which form the outer cuticle layer. Both the hydrophobic nature of the fibre surface and the high cross-linking density of the protein layer immediately below the lipid layer act as a natural diffusion barrier. This can complicate wool finishing processes and can necessitate a modification of the fibre surface by applying special auxiliaries and, in some cases, acid chlorination.

Scientific and technical progress, which is closely linked to innovative potential and to technological know-how, is the key for sustainable growth. Due to their broad application potential in almost all areas, surface modification techniques are an important factor in developing key technologies. Surface technologies offer a virtually unlimited potential for modifying the surface characteristics of a material in accordance with its specific requirements. Low-temperature plasmas (barrier and glow discharges) are of special interest, not only to replace less environmentally friendly finishing processes but also to create new surface characteristics and thereby open up new fields of application for various materials. Though being already established in many areas of industry, low-temperature plasmas are being explored for their application in the textile industry due to particular advantages which can be expected for different uses. Therefore, in the last decade, the plasma-induced modification of natural and man-made fibre surfaces has been investigated in different fields of applications for clothing and technical textiles.

Apart from inducing permanent hydrophilicity, fibre matrix adherence in fibre-reinforced composites and fibre protection towards chemical attack and soiling in technical textiles, the application of low-temperature plasmas can significantly influence the finishing and usage properties of clothing textiles. In particular, for wool finishing, plasma technology offers an enormous potential ranging from improved dyeing, printing and spinning performance to reduced felting tendency. Since concern for the environment and introduction of strict ecological legislation has caused environmental pressure on industry, the application of low-temperature plasmas to wool has recently become of increasing interest, particularly with regard to an improvement of dye-uptake and to replace the chlorination stages in commercial shrink proofing and printing.

9.2 Plasma systems relevant for application to wool

Low-temperature plasmas (barrier- and glow-discharge plasmas), which are only relevant to textile applications, are characterised by a thermal non-equilibrium between heavy particles (ions, metastables, neutrals) and light particles (electrons). With these plasmas, surfaces can be modified at low temperatures, an effect which is related to the low temperature of heavy particles combined with high electron energies that are typically found in low-temperature plasmas.[1]

The barrier discharge (BD) plasma is characterised by a low current discharge under atmospheric conditions, generated by application of high voltages. Barrier discharges consist of transient micro-discharges whose distribution can be controlled by matched voltage wave forms.[2] Insulators, at least at one of the electrodes, prevent an electrical breakdown which would lead to the formation of an arc and burns the substrate. In order to discharge a corona under atmospheric conditions, a high electrical field at one electrode has to be generated. Electrons leaving the electrode are accelerated by a high voltage in the direction of the insulator, which is situated immediately below the material to be treated. On their way to the substrate, the electrons collide with air molecules leading to the formation of ozone and nitrogen oxides. Those electrons which hit the counter electrode have high energies (average energy level: 5 eV[3]) and are able to split covalent linkages in the surface of the substrate, resulting in the formation of radicals. Their subsequent reaction with products in the corona atmosphere leads to a surface specific oxidation.

In contrast to the BD plasma, the glow-discharge plasma (GD) generally operates at reduced pressures (10^{-3}–10^{-4} bar) at lower voltage inputs and is characterised by a higher current discharge. As a consequence of the low pressure, the electron energies are higher when compared to barrier discharges (up to 10 eV), resulting in a faster and deeper surface modification. In addition, the electron densities in radio frequency- and microwave-induced GD plasmas were known to be many times higher than that of a BD plasma. The same relationship exists for the concentration of active particles produced in such discharges. A GD plasma it is therefore expected to assist in achieving the desired results in much shorter treatment times. Furthermore, the mean free paths of reactive plasma species are higher when compared to those generated at atmospheric conditions. This results in a more complete surrounding of each individual fibre by the plasma, leading to a more even modification, especially when higher weight fabrics, yarns or tops are treated. Voluminous wool tops can therefore be more evenly treated in their delivered form with GD, whereas homogenous treatment results with BD require a reduction of the original top weight by drafting as well as by a double-sided treatment.[4,5] However, the main advantage of BD over GD is that wool can be treated at atmospheric pressure, thus avoiding the use of low-pressure equipment.

Apart from other plasma systems constructed for textile treatment, there are two plasma systems which have been mainly developed for the treatment of wool that allow a larger scaled continuous air-to-air-treatment. In the 1980s, Rakowski[4] developed a continuous operating machine for the application of GD on wool top. This system operates at 13.56 MHz and is fitted with a four-step vacuum system to achieve and keep a pressure of 50 Pa during a production rate of up to 10 m/min. At the end of the last century, Softal[5] developed a continuous operating machine for wool using atmospheric pressure dielectric barrier discharges (DBD), which can be coarsely regarded as a further development of the machinery described by Belin in 1976.[6] The DBDs in this system are generated in the plasma unit between parallel arranged ceramic-coated roller electrodes by application of pulsed high alternating voltages. The station is designed for a double-sided treatment of wool consisting of two motor-driven, earthed backing rolls and rotating electrode rolls connected to the high voltage. The wool is guided between the electrodes and is penetrated by the discharges perpendicular to the transportation direction of the substrate. The system allows treating both, wool tops and fabrics. For top treatment, a spreading unit enabling a simultaneous treatment of 16 tops is connected to the inlet and to wool top containers at the outlet of the plasma unit. For full-scale fabric treatments, a batch unwinder with a fabric spreading and guiding system at the inlet and a batch winder at the outlet of the plasma unit can be implemented.[5,7]

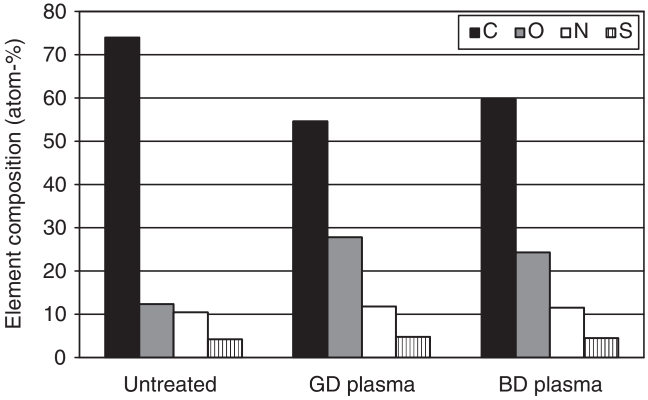
9.3 Plasma-induced chemical and morphological changes

Wool has a very complex fibre surface which is responsible for the majority of wool properties, such as water repellence, soil resistance, resistance to chemical attack and felting behaviour. The fibre surface (cuticle) shows a characteristic scale structure, built of flattened cells overlapping each other. The cuticle can be subdivided into four coaxial layers of different chemical composition: (i) the outermost hydrophobic epicuticle, mainly consisting of covalently bound fatty acids, (ii) the exocuticle immediately below the epicuticle, which is divided into an A- and B-layer and is highly cross-linked via cystine bridges, (iii) the less cross-linked endocuticle beneath the exocuticle and (iv) the cell membrane complex (CMC), a proteinaceous membrane between cuticle and cortex.

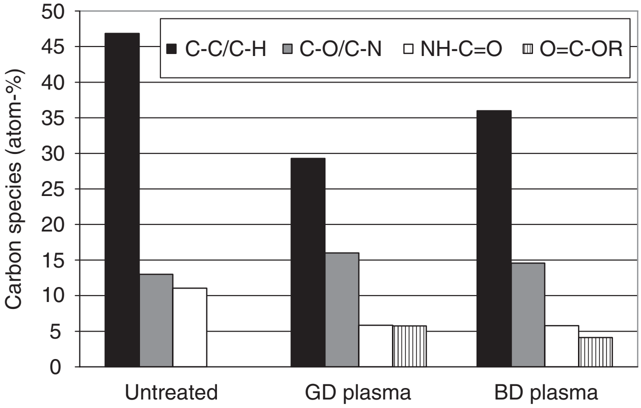
Though the hydrophobic nature of the fibre surface and the high cross-linking density in the outermost fibre surface act as a diffusion barrier and protect the native wool fibre from environmental influences, wool finishing processes can be complicated by the natural structure of the cuticle. Therefore, in wool finishing processes, such as printing, dyeing or shrink-proofing, surface modification plays an important role. To date, the required surface modification is mainly accomplished by wet chemical processes using special auxiliaries or chemical surface oxidation, e.g. the chlorination processes. An appropriate alternative to conventional treatments is given by the pre-treatment of wool with low temperature plasmas (LTPs).

A number of investigations into the effect of plasma treatments on wool have shown that the observed changes in finishing and care performance of wool are related to surface-specific changes of the protein fibre by the plasma treatment. Surface analyses of wool fibres treated with different plasma gases have shown that the content of hydrophilic groups increases and that part of the cystine in the surface layer is converted to cysteic acid.[8–12] The increase in hydrophilic groups is based on surface oxidation during LTP treatment. The surface oxidation can be regarded as the consequence of water desorption from the fibre during the plasma treatment, resulting in a predominant presence of oxygen and its highly energetic (reactive) derivatives in the discharges, even when inert gases are used as reaction gases. However, the resulting degree of surface oxidation strongly depends on the reaction gas used and increases significantly when oxygen-bearing gases are used instead of N_2, Ar and H_2, respectively.[10,13,14] This applies for LTP treatment both at reduced pressure and under atmospheric conditions.[13,14] In addition, the resulting degree of surface oxidation depends on the type of plasma applied.

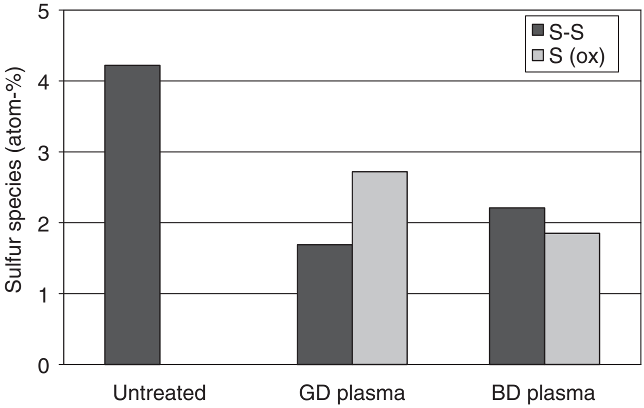
Conventional amino acid analyses of plasma-treated wool reveal only little change because reaction is restricted to the fibre surface.[10] Chemical changes can be detected by surface-sensitive X-ray photoelectron spectroscopy (XPS) being able to provide elemental analysis and determination of the binding state of the elements at the wool surface and in the immediate subsurface down to a depth of about 10 nm. In the XPS survey spectrum peaks related to carbon, oxygen, nitrogen and sulphur are observed.[9,10,13,14] As shown in Figure 9.1, plasma treatments cause changes in the chemical composition of the wool fibre surface, an effect that is mainly related to a decrease in carbon content, whereas increasing amounts of oxygen, nitrogen and sulphur are detected to an extent that is more intensive for GD than for BD treatments. The high-resolution carbon spectra show that the aliphatic carbon species are significantly reduced by the action of plasma. Figure 9.2 shows that the strongest changes are observed, as expected, for



9.1 Changes in the element composition of the wool fibre surface after application of GD and BD plasma.



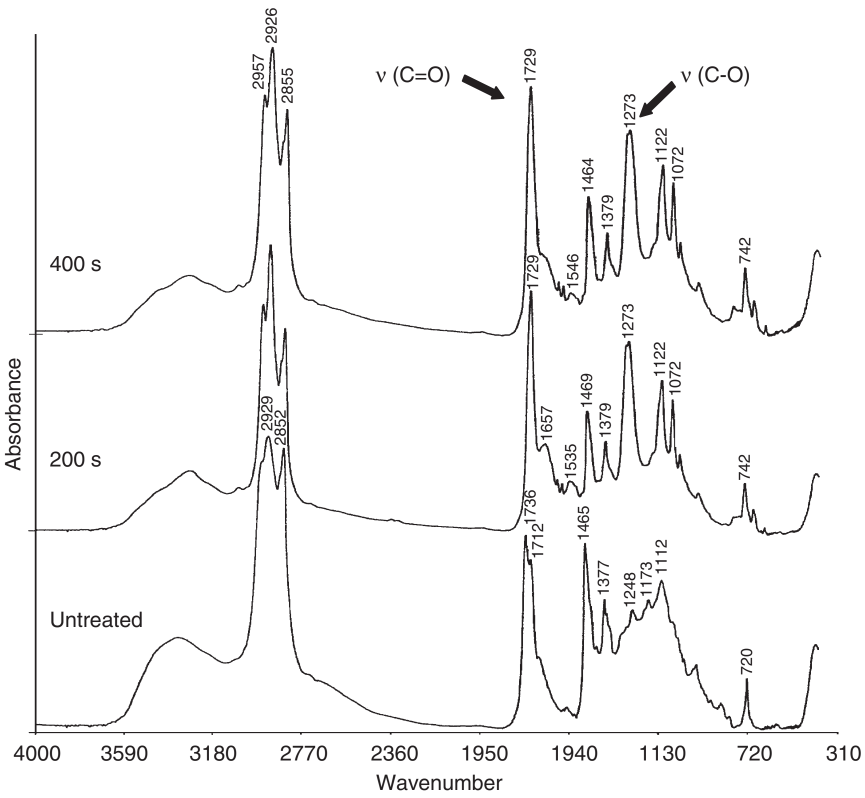
9.2 Changes in the content of carbon species of the wool fibre surface after application of GD and BD.



9.3 Changes in the content of sulphur species of the fibre surface after application of GD and BD to wool.

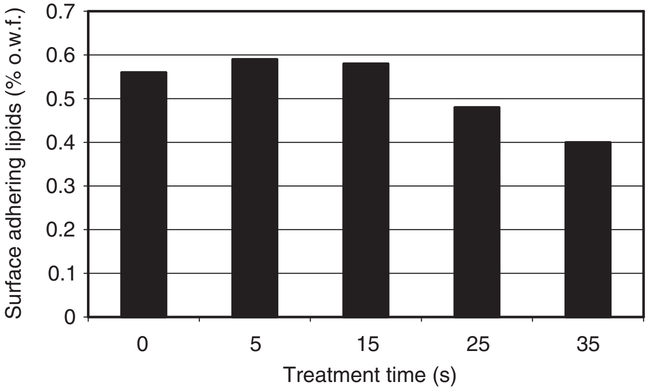
the GD-treated samples. The decrease in aliphatic carbon is associated with an oxidation of sulphur, present in disulfide linkages, to sulfonic acid groups. As shown in Figure 9.3, the oxidation of cystine residues present in the A-layer of the exocuticle is more complete after treatment of wool with GD than the corresponding changes detected after treatment with BD.

The application of oxygen-bearing plasmas results first of all in an oxidation of adhering and covalently fixed surface lipids. This counts for both plasma treatments and is demonstrated in the IR spectra of adhering lipids isolated from glow-discharge treated wool showing a strong increase in the amount of carbonyl as well as single-bonded CO groups (Figure 9.4). In addition to the changes detected by IR spectroscopy, a decreasing amount

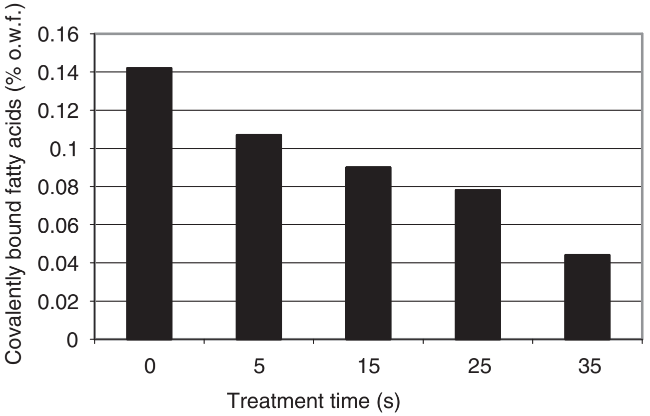


9.4 IR spectra of extracted surface-adhering lipids before and after GD plasma treatment.

of surface lipids is observed with increasing treatment time, indicating a plasma-induced removal of surface lipids by etching. This applies to both plasma treatments investigated and is exemplified in Figures 9.5 and 9.6, for surface lipids isolated from BD-treated wool. To identify the reaction pathways of plasma-induced lipid oxidation, Merten[13] analysed model lipids after glow discharge treatment. The weight determination of plasma-treated icosanoic acid, palmitic acid, 19-methylicosanoic acid, triolein and cholesterol showed that the etching rate decreases with increasing molecular mass of the lipid. As determined by IR spectroscopy and mass spectrometry (MALDI-MS), the initial step of lipid degradation is an oxidation of the aliphatic hydrocarbon chain resulting in the formation of carboxylic groups, which are also detected in fatty acids isolated from plasma-treated wool (Figure 9.4). In the case of ramified hydrocarbon chains (e.g. 18-methylicosanoic acid), the oxidative degradation and subsequent formation of carboxyl groups is initiated mainly at the tertiary carbon.



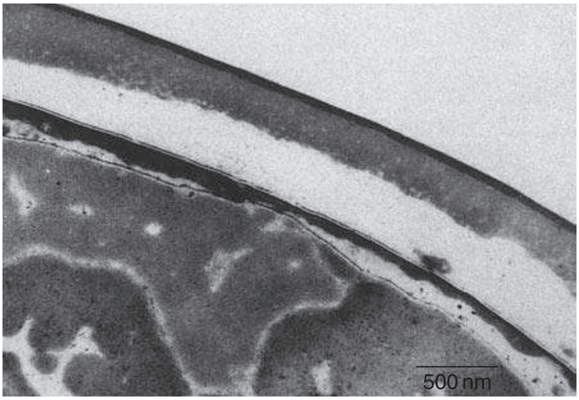
9.5 Amount of surface-adhering lipids as a function of the treatment time in BD (determined by solvent extraction and subsequent weight determination).



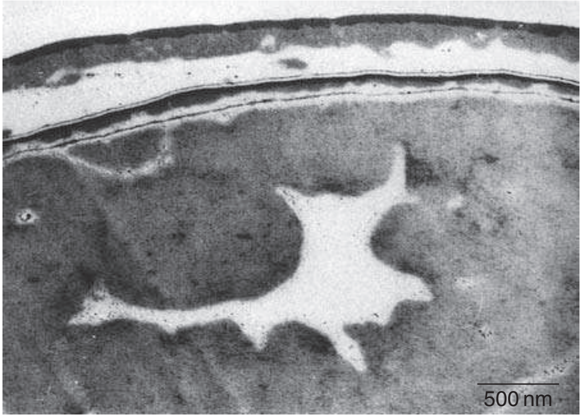
9.6 Amount of covalently bound fatty acids as a function of the treatment time in BD (determined by gravimetry after isolation via transesterification).

Scanning electron microscopic (SEM) images show no noticeable differences when compared with the corresponding untreated samples. The extent of surface modification can be visualised by transmission electron microscopy (TEM) of fibre cross-sections. As shown in Figures 9.7–9.9, a plasma treatment modifies the A-layer of the cuticle, indicating that the degree of modification depends on the plasma technique applied.

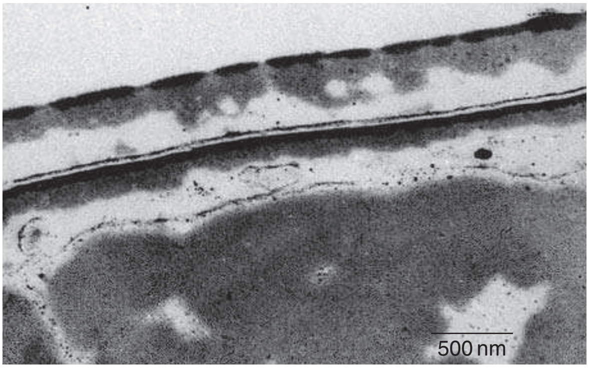
Figure 9.7 shows an electron micrograph of the untreated fibre with its untouched cuticle region. The extent of plasma-induced surface modification is demonstrated in Figure 9.8 for a BD-treated sample and in Figure



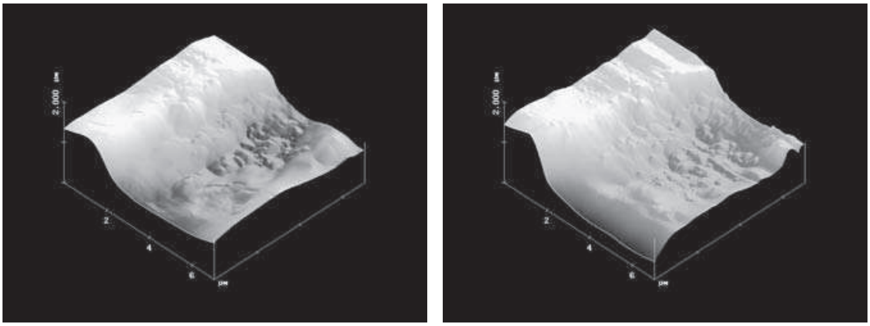
9.7 TEM image of an untreated wool fibre.[22]



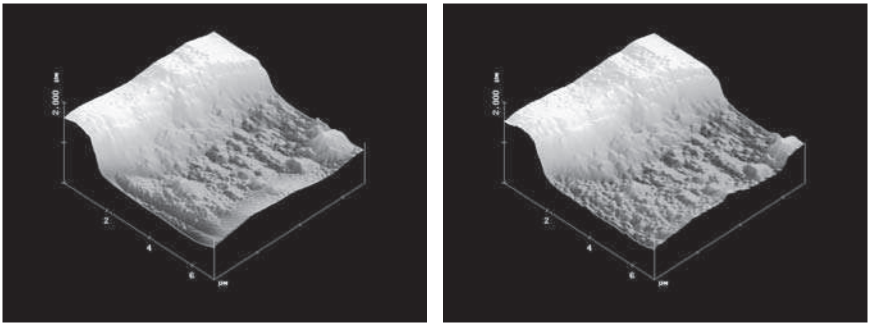
9.8 TEM image of a DBD-treated wool fibre.



9.9 TEM image of a GD-treated wool fibre.[22]



(a) Untreated (b) 100 s



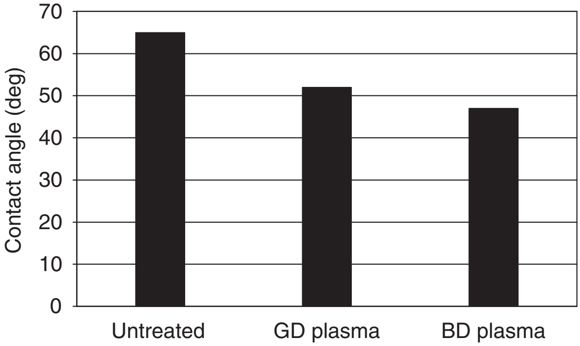
(c) 200 s (d) 300 s

9.10 AFM images of the same section of a wool fibre surface with different exposure times to GD.[13]

9.9 for a corresponding GD-treated fibre. From these pictures it becomes evident that a plasma treatment can modify the A-layer of cuticle to varying degrees, resulting in a partly considerable swelling. In contrast to the application of BD, the staining intensity in GD-treated fibres (Figure 9.9) is in places considerably reduced, and parts of the A-layer have been sputtered off, leading to the formation of grooves in this layer. This underlines (i) the influence of more reactive species present in this type of plasma, and (ii) that chemical reactions induced by the action of reactive plasma species can be accompanied by etching of the fibre surface, resulting in a rougher and larger surface area. The latter is corroborated by images from atomic force microscopy (AFM) which reveal more surface detail of the plasma-treated wool samples (Figure 9.10).

9.4 Textile properties of plasma-treated wool

The partial removal of surface lipids, the increase in carbonyl and single-bonded CO groups, the conversion of cystine to cysteic acid in the fibre



9.11 Influence of the plasma treatment on wettability of wool. (Contact angle measurements according to Wilhelmy[37].)

surface and the increase in surface roughness results in an increase in the wettability of wool. As expected, the magnitude of wettability is higher for the GD-treated sample when compared to the corresponding data determined for BD-treated wool (Figure 9.11).

Apart from the wettability increase, the plasma-induced surface oxidation is accompanied by a decreased handle performance and higher fibre–fibre friction. As demonstrated by Ryu and Wakida,[15] the dry and wet frictional coefficients of plasma-treated wool fibres are significantly increased in the with- and against-scale directions to an extent which is higher for the GD- than for the BD-treated samples. For GD-treated wool tops, Rakowski[4] has shown that the dry and wet frictional differences in both scale directions are reduced.

Felting is a special property of wool that occurs when wool is subjected to mechanical agitation in water. Though this behaviour is required for creating felts or fabrics with special optical appearance, the well-known irreversible shrinkage during washing is one of the principal drawbacks of textiles made of wool. Felting and shrinkage are the result of movements of individual fibres within the textile, always taking place towards the fibre root. The phenomenon of unidirectional fibre movement primarily is related to the unique scale structure (from the root to the tip) of the wool fibre surface, which is responsible for a different coefficient of friction in the with-scale and against-scale direction. As a consequence of the reduction in the difference in the coefficient of friction, plasma-treated wool shows a significantly diminished felting behaviour.[4,5,13–17]

In addition to the reduced felting behaviour of wool, the increase in fibre friction after application of GD or BD leads to an increased cohesiveness of plasma-treated wool fibres, resulting in considerably improved abrasion resistance, sliver tenacity and yarn strength.[4,6,18,19] According to Rakowski,[4] the latter is improved to an extent of 16% when compared to the corresponding values determined for yarns of the untreated material. Since fibre strength measurements on plasma-treated wool indicate that the action of reactive plasma species is strictly restricted to the fibre surface and do not alter the fibre quality,[17] this allows the generation of finer yarns and thus, of lighter weight textiles from wool at a high quality level.

9.5 Finishing performance of plasma-treated wool

9.5.1 Dyeing and printing behaviour of plasma-treated wool

From the work of Leeder and his co-workers who could follow the uptake of pre-metallised dyes by wool via TEM, it is evident that, due to the virgin diffusion barrier, the dye molecule does enter the untreated fibre via cuticle cell junctions.[20] However, it is not the same for plasma-treated wool. Light microscopic studies of the initial stage of the dyeing process with Sulforhodamine G showed significant differences between untreated and plasma-treated wool. Whereas in the case of the untreated wool the dye almost selectively stained the outer scale edges in accordance with the results reported by Brady,[21] no such concentration of dye in these regions was observed for the plasma-treated fibre.[22] Instead, already in this initial dyeing stage, a staining of the cuticle scales extending from the scale edges to the ends of the scales was observed. Examinations on fibre cross-sections of correspondingly treated samples showed that plasma-treated wool is more easily penetrated by the dyes, which were more evenly distributed over the cross-sections.[22] This can be attributed to the plasma-induced removal of surface lipids and to cystine oxidation in the A-layer of the exocuticle, and thus to a degradation of the natural diffusion barrier in the fibre surface, which obviously facilitates the transcellular dye diffusion besides the intercellular dye diffusion postulated for the untreated wool.[20]

The improved dye-uptake of plasma-treated wool described by different authors[4,7,15,18,22–28] can be therefore related to the plasma-induced degradation of the natural diffusion barrier of the fibre. This obviously facilitates an accelerated, more even and more complete dye-uptake, resulting in significant enhanced final bath exhaustion and thus in significantly reduced effluent discharges during dyeing. The latter is concluded from analyses of effluents from industrial dyeing trials with chromium-bearing 1:1-premetallised dyes.[7] As shown in Table 9.1, a considerable reduction in chemical (COD) and biochemical (BOD_5) oxygen demand is detected in the exhausted dye-bath from the DBD-treated fabric. Since this is further accompanied by a reduced chromium content and translucent coloration number, the detected reduction in COD and BOD_5 load of the effluent is obviously partly caused by a more complete dye-uptake of the DBD-treated

Table 9.1 Effluent load of the exhausted dye-baths from DBD treated and untreated wool fabrics during industrial dyeing with 1:1-premetallised dyes under comparable conditions

	Untreated fabric			DBD treated fabric		
COD	12 500 mg/l			6500 mg/l		
BOD_5	852 mg/l			1170 mg/l		
COD/BOD_5	14.67			5.56		
Translucent coloration number	*620 nm*	*525 nm*	*436 nm*	*620 nm*	*525 nm*	*436 nm*
(DFZ) (ε at $d = 1$ m)	40.0	31.6	30.7	25.2	13.2	8.1
Cr_{total} after digestion	1.97 mg/l			1.84 mg/l		

fabric when compared to that of the non-pretreated reference. As a consequence of the improved dye-bath exhaustion, the final shade of the DBD-treated fabric appears darker than that of the correspondingly dyed reference material,[7] clearly indicating that a plasma-treated fabric may require less amount of dyestuff for a given shade. Since dye exhaustion strongly depends on the initial dye concentration, a reduction in the amount of dye used will potentially further contribute to a diminished effluent load.[7]

Due to the low permeability to dyes, wool shows only poor printability. Thus, in order to satisfactorily print wool, it is necessary to prepare the wool for printing by degradation of the virgin diffusion barrier. This is traditionally achieved by mild chlorination. Due to the resulting effluent load with adsorbable organic halides (AOX), there is a quest for environmentally more acceptable print-preparation processes. For this reason, plasma treatment of wool has also been investigated with special regard to its potential to replace the conventional chlorination techniques. For this purpose the effects of differently intensive BD- and oxygen-atmosphere GD-treated fabrics on the resulting printability with colour pastes of acid dyes have been elucidated.[15] Whereas the dye-uptake during subsequent steaming increases with the treatment intensity, the resulting colour depth decreased, thus indicating that only a slight surface modification with BD is particularly effective for printing of wool fabrics.[15] Further, BD-treated wool fabrics can meet the colour depth of conventionally chlorinated samples during printing.[29] The results shown in Table 9.2 demonstrate the improved depth of shade (L*) after printing with an acid milling dye, to an extent which meets the corresponding values for the chlorinated sample. This clearly underlines the propensity of plasma treatments for imparting printability to wool and thus, the feasibility of replacing conventional chlorination processes for print preparation.

Table 9.2 Colour development (CIE values) after printing of differently pretreated fabrics with an acid milling dye

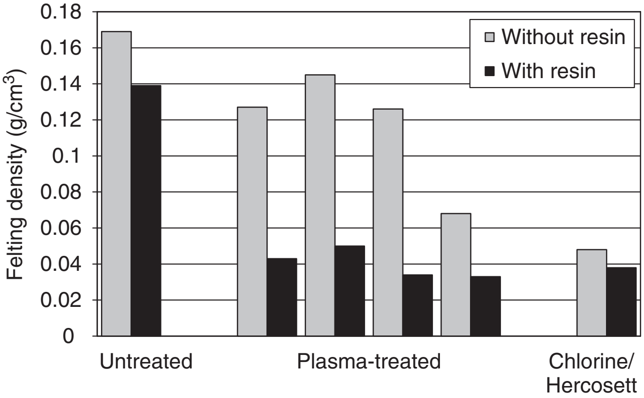
Pretreatment	CIE-values			
	L*	A*	B*	ΔE
Untreated	31.3	–0.7	–23.4	0
Chlorinated	26.5	–2.0	–25.8	3.51
CD-treatment	26.8	–2.4	–25.7	3.80

9.5.2 Plasma-induced shrinkproofing of wool

Apart from print preparation, commercial shrinkproofing causes tremendous environmental problems by using chlorine as an oxidising agent. Today, nearly 75% of the overall production of machine-washable wool is carried out at the stage of wool top being the base material for yarn production. State-of-the-art so far is the Chlorine/Hercosett treatment, a continuously operating combined process using chlorination as a preliminary step to polymer coating of the fibre with a polyaminoamide (Hercosett). The disadvantage of this process is again its contribution to the overall discharge of AOX in effluents. Chlorinated organic substances are recognised as being mostly toxic, and a number of countries have established maximum concentration levels for these compounds in effluents. Since the AOX generation during conventional shrinkproofing of wool exceeds the permitted levels by up to 40 mg/l,[30] an environmentally acceptable, chlorine-free process for imparting full machine washability is required.

For shrinkproofing of wool, a plasma-induced surface oxidation as well as a direct coating of the fibres by plasma polymerisation is found also to reduce, but not to eliminate, felting. Since plasma polymers deposited on wool fibres are known to decrease the dye uptake by the fibre,[31,32] a plasma polymerisation does not meet the requirements for treatments at the stage of top. Therefore, generation of non-shrinkable wool has been mainly concentrated on the plasma-induced surface oxidation. This requires an additional coverage of the fibre surface to further decrease the difference in coefficient of friction by masking the scale edges. Since commercially available resins do not show the expected positive influence on the felt-free performance of plasma-treated wool, new resins have been tailored for the plasma-treated fibre surface.[7,33]

Two different wool-compatible resin types have been developed by BAYER, allowing the generation of machine-washable wool after GD or BD treatment. One type consists of a water-dispersible isocyanate-bearing resin which is able to permanently coat each individual fibre. As a consequence, the scale heights of the fibre surface are significantly reduced,



9.12 Felting densities (IWTO 20-69) of differently plasma-treated wool before and after resin application in comparison to the corresponding data for the untreated and Chlorine/Hercosett treated material.

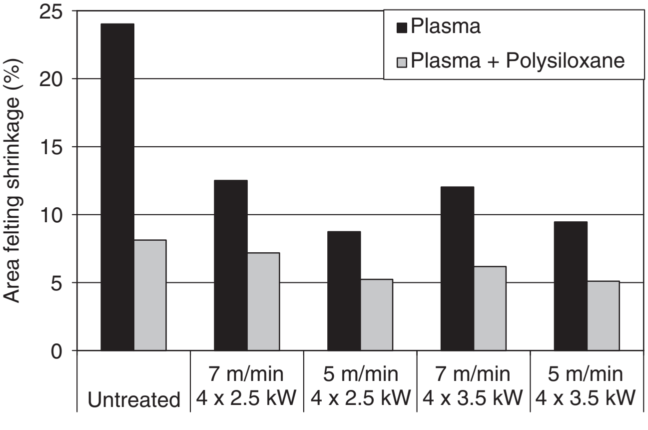
resulting in nearly equalised with- and against-scale friction values.[17] As shown in Figure 9.12, the differences in the degree of felting observed after different plasma-only treatments can be equalised by the resin application, to an extent which meets the value correspondingly determined for Chlorine/Hercosett-treated samples. The second resin is a polyurethane type which does not coat the fibre completely, but is deposited at the scale edges instead. This also results in significantly decreased shrinkage behaviour. DBD treatment of tops followed by application of one or both resins guarantees the specifications set by the Woolmark Company in their Technical Method 31 (TM 31). This requires that the area felting shrinkage of knitted fabrics must not exceed a value of 10% after 50 simulated washing cycles in a domestic washing machine. With a reduction in area felting shrinkage from 69% for the untreated and over 21% for the DBD-treated, to 1–3% for the additionally isocyanate- or polyurethane-treated samples, this can be completely fulfilled. The result has led to the development of a completely AOX-free shrinkproofing process for wool tops[5,17,33] and has thus opened up a new possibility for the wool industry to have an environmentally acceptable, plasma-based shrinkproofing process in the near future.

9.5.3 Softening of plasma-treated wool

The oxidation of surface lipids, and their partial removal, results in poor handling performance to some extent, which requires an additional softening of plasma-treated wool. Investigations on commercially available softeners of different chemical compositions (cationic and non-ionic fatty acid condensates with and without polysiloxane additions, fatty acid amides and polyethylene derivatives, cationic polysiloxanes as well as reactive aminosiloxanes) have shown that a softening step can interfere with the plasma-induced antifelt finish.[7] Though most of the softeners improved the handle performance significantly, the plasma-generated antifelt-finish is simultaneously decreased by softening to an extent that exceeds the felting tendency of the untreated material.[7]

One reason for the increased felting tendency of plasma-treated wool by softening is the increase in hydrophobicity. As a consequence of the hydrophobic effect, the fibres aggregate in aqueous medium and, under mechanical action, move to their root end to form a felt. The second reason is the reduction in fibre–fibre friction, thus allowing an increased movement of the individual fibres towards to their root, which further contributes to an increase in felting behaviour. Since the plasma-induced shrinkproofing effect is mainly based on (i) a hydrophilisation of the fibre surface and (ii) an increase in fibre–fibre friction, the application of softeners was believed to be incompatible with a plasma-induced shrinkproofing effect.

The only exception from this general trend determined for a series of softeners was given for softeners which were able to coat the fibre surface permanently and thus, to further reduce the differential friction coefficient. This was shown for a reactive aminosiloxane, which was able to additionally reduce the felting behaviour of plasma-treated wool (Fig. 9.13).[7] From these actual results, it can be concluded that a plasma-induced antifelt finish for wool is not necessarily accompanied by a non-reparable decrease in handling performance. Softeners being able to coat the fibre have the potential to overcome this well-known problem.



9.13 Influence of the plasma, and subsequent treatment with a reactive polysiloxane, on the felting behaviour of wool fabrics at various power-inputs and production speeds during DBD-treatment.

9.6 Future trends

Plasma treatment leads to selective modification of the outermost wool fibre and has many implications for improved dyeing, printing, shrinkproofing and subsequent chemical finishing. Plasma treatments of wool represent a most innovative approach to replacing chlorination stages in wool finishing and to improving existing processes with special regards to an economical–ecological optimisation. The apparent potential of plasma technology for wool finishing processes led to the development of machinery allowing a treatment under atmospheric conditions for different fibre make-ups. This can be regarded as a large step towards industrial implementation that will help the wool industry to benefit in the near future from a technology that is extremely surface-specific, totally effluent free, and thus less destructive and more environmentally friendly. The implementation of plasma technology into the wool industry is closely connected to further developments towards larger-scaled machinery, allowing a cost-efficient treatment with special regards to a high material throughput, as well as to the development of highly efficient tailored auxiliaries for achieving special effects.

9.7 Sources of further information

For readers who wish to obtain more detailed information about wool, only a few key books can be advised describing the wool fibre science and technology from the morphological to the chemical and finally to the technological point of view of this exciting fibre material.[34,35,36] Wool science is continuing to grow, leading to new innovations. The status quo on actual developments of experts all around the world is presented at the International Wool Conference, which takes place every 5 years and was last held in 2005 in Leeds, UK. The proceedings of these conferences, as well as the relevant journals, are of special interest to readers searching for special topics.

9.8 Acknowledgments

Thanks are due to Deutscher Fachverlag GmbH for permission to reproduce the photographs shown in Figures 9.7 and 9.9.

9.9 References

1. Drost H (1978), *Plasmachemie*, Berlin, Akademie.
2. Reitz U (1992), *Barrierenentladungen zur plasmagestützten Oberflächenbehandlung*, PhD-thesis, TU Braunschweig.

3. Kogelschatz U, Eliasson B, Egli W (1997), 'Dielectric barrier discharges, principle and applications', *Journal de Physique* **7**, C4–47.
4. Rakowski W (1989), 'Plasma modification of wool under industrial conditions', *Melliand Textilber.* **70**, 780–785.
5. Förster F, Prinz E, Martens B (2000), 'Basic investigations on atmospheric pressure barrier discharges for shrinkproofing of wool tops', *Proc. 10th Int. Wool Text. Res. Conf.* Aachen(D), PL-5.
6. Belin R E (1972), 'The effect of corona treatment on the cohesion between fibres and on their wettability', *J. Text. Inst.* **67**, (7/8), 249–252.
7. Thomas H, Lehmann K-H, Höcker H, Möller M, Thode C, Lindmayer M (2005), 'Plasma pre-treatment at atmospheric conditions for improved processing and performance characteristics of wool fabrics', *Proc. 11th Int. Wool Text. Res. Conf.* Leeds (UK).
8. Millard M M (1975), 'Surface analysis of plasma treated wool fibres by X-ray photoelectron spectrometry', *Proc. 5th Int. Wool Text. Res. Conf.* Aachen (D), II, 44–53.
9. Pavlath A E, Lee K S (1975), 'Wool modifications induced by low temperature glow discharge', *Proc. 5th Int. Wool Text. Res. Conf.* Aachen (D), III, 263–274.
10. Klausen T (1995), *Einfluss von Niedertemperaturplasmen auf die Chemie und Morphologie der Wollfaseroberfläche*, PhD-thesis, RWTH Aachen.
11. Kaufmann R, Herrling J, Thomas H, Klausen T, Höcker H (1993), 'Neue Erkenntnisse zur Oberflächenmodifizierung von Wolle mit Plasma (Corona- und Glimmentladung). Teil 1: Charakterisierung', *DWI-Reports* 111, 297–313.
12. Thomas H, Herrling J, Rakowski W, Kaufmann R, Höcker H (1993), 'Neue Erkenntnisse zur Oberflächenmodifizierung von Wolle mit Plasma (Corona- und Glimmentladung). Teil 2: Praktische Bedeutung', *DWI-Reports* 111, 315–326.
13. Merten T (1998), *Einsatz von Niedertemperatur-Plasmen zur Filzfreiausrüstung von Wolle*, PhD-thesis, RWTH Aachen.
14. Monser V (2001), *Behandlung von Wolle in Barrierenentladungen*, PhD-thesis, RWTH Aachen.
15. Ryu J, Wakida T, Takagishi T (1991), 'Effect of corona discharge on the surface of wool and its application to printing', *Textile Res. J.* **61**, (10), 595–601.
16. Pavlath A E, Lee K S (1975), 'Effect of afterglow on the felting shrinkage of wool', *Textile Res. J.* **45**, 742–745.
17. Thomas H, Merten T, Monser V, Höcker H (2000), 'Fundamentals of plasma-supported shrinkproofing of wool: selective modification of the fibre surface and resulting technological consequences', *Proc. 10th Int. Wool Text. Res. Conf.* Aachen (D), PL-3.
18. Pavlath A E, Slather R F (1971), 'Low temperature plasma chemistry. I. Shrinkproofing of wool', *Appl. Polym. Sympos.* Part II, **18**, 1317–1324.
19. Lee K S, Pavlath A E (1974), 'Low temperature plasma treatment of wool. II. Effect of variables on shrinkage and yarn strength', *J. Polym. Sci.* **12**, 2087–2090.
20. Leeder J D, Holt L A, Stapleton I W (1990), 'Diffusion of dyes and other reagents into the wool fibre', *Proc. 8th Int. Wool Text. Res. Conf.* Christchurch (NZ), IV, 227–238.

21. Brady P R (1990), 'Penetration pathways of dyes into natural protein fibres', *Proc. 8th Int. Wool Text. Res. Conf.* Christchurch (NZ), IV, 217–226.
22. Höcker H, Thomas H, Küsters A, Herrling J (1994), 'Färben von plasmabehandelter Wolle', *Melliand Textilber.* **75**, (6), 506–512.
23. Lee M, Ryu J, Wakida T, Lee M S, Pak K P, Chen J (2001), 'Dyeing transition temperature of wools treated with a low temperature plasma, liquid ammonia, and high-pressure steam in dyeing with acid and disperse dyes', *J. Appl. Polym. Sci.* **80**, (7), 1058–1062.
24. Thomas H, Höcker H (2002), 'Textile uses for plasma technology', *Wool Record* **161**, (3688), 38–39.
25. Thomas H, Herrling J, Rakowski W, Höcker H (1993), 'Umweltfreundliche Veredlungsverfahren für Wolle durch Vorbehandlung mit elektrischen Gasentladungen', *Intern. Text. Bulletin* **39**, (2), 42–29.
26. Thomas H, Höcker H (1995), 'Plasma treatment of wool with special regard to the dyeing properties', *Proc. 9th Int. Wool Text. Res. Conf.* Biella (I), IV, 351–357.
27. Lee M, Wakida T (1992), 'Dyeing property of plasma-treated wool with direct dyes', *Sen'i Gakkaishi* **45**, (12), 699–703.
28. Wakida T, Tokino S, Niu S, Lee M, Uchiyama H, Kaneko M (1993), 'Dyeing properties of wool treated with low-temperature plasma under atmospheric pressure', *Textile Res. J.* **63**, (8) 438–442.
29. Thomas H, unpublished results.
30. Müller B M (1992), 'Adsorbable organic halogens in textile effluents', *Rev. Prog. Colouration* **22**, (1) 14–21.
31. Goto T, Wakida T, Hosotani T (1991),'Effect of low temperature plasma treatment on dimensional stability of wool fabrics', *Sen'i Gakkaishi* **47**, (7), 358–364.
32. Ryu J, Dai J, Koo K, Wakida T (1992), 'Dyeing property of wool treated with low temperature plasma', *Sen'i Gakkaishi* **48**, (5) 213–220.
33. Jansen B, Kümmeler F, Thomas H, Müller H-B (2000), 'New resins for shrinkproofing of plasma-treated wool', *Proc. 10th Int. Wool Text. Res. Conf.* Aachen (D), PL-6.
34. Simpson W S, Crawshaw G (2002), *Wool: Science and Technology*, Cambridge, Woohead Publishing Limited.
35. McLaren J A, Milligan B (1981), *Wool Science: The Chemical Reactivity of the Wool Fibre*, Marrickville, Science Press.
36. Fraser R D B, MacRae T P, Rogers G E (1972), *Keratins: Their Composition, Structure and Biosynthesis*, Springfield, Thomas.
37. Wilhelmy J (1863), 'Über die Abhängigkeit der Capillaritäts-Constanten des Alkohols von Substanz und Gestalt des benetzten festen Körpers', *Ann. Phys.* **195**, 177–217.

10

Plasma modification of natural cellulosic fibres

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10.1 Introduction

This chapter provides a general summary of the current state of knowledge of plasma modification of various natural cellulosic fibres. Much of the information reported here is taken from the references cited at the end of the chapter, which should be consulted for a more in-depth treatment. Several aspects of plasma modification of various natural cellulose fibres are thoroughly treated in a number of excellent works.[1,2]

Although the literature is abundant with descriptions of plasma-enhanced synthesis of macromolecular structures and surface modification of synthetic polymeric substrates, plasma treatment of natural macromolecular compounds has received less attention for the following reasons:

- The abundance, low cost, and availability of petrochemical precursors of synthetic polymers during and after World War II
- The remarkable physiochemical characteristics (processability, chemical inertness, mechanical strength, etc.) of synthetic polymers.

However, an increasing awareness of the benefits and advantages of lignocellulosics, which are the most significant renewable natural polymeric resource, has increased the interest in improving their surface properties further using plasma surface modification. A brief presentation of various cellulosic fibres (Section 10.2) is followed by a section devoted to exploring the mechanisms of the interaction between various plasmas and cellulosic fibres, including generation of free radicals and oxidation of cellulose surfaces using argon and oxygen plasmas (Section 10.3). Section 10.4 deals with plasma modification of cotton fibre, which is the purest cellulosic fibre, for improved surface properties in various textile applications.

The lignocellulosics, especially various vegetable fibres, are natural composites built up of cellulose and lignin and are light-weight, strong, abundant, biodegradable and relatively inexpensive, which makes them ideal components for creating advanced materials in conjunction with synthetic thermoplastic polymers. High lignocellulosic-content composites combine the attributes of natural macromolecules (e.g. supramolecular order, non-hazardous, renewability) with the chemical inertness, processability, high tensile strength, etc. characteristics of the synthetic counterparts. Section 10.5 describes how plasma surface modification of the lignocellulosic fibres (and also the thermoplastic counterpart) can improve the mechanical and adhesion properties of the resulting composite.

Plasma surface modification of solid wood and wood pulp fibres is discussed in Section 10.6 and the final section deals with plasma modification of regenerated cellulose fibres such as, for example, cellophane and rayon viscose fibres.

10.2 Description of natural and man-made cellulosic fibres

This section provides a short description of the different types of cellulosic fibres as they appear in this chapter.

10.2.1 Cellulose

Cellulose is the most widely known fibrous polysaccharides and it occurs in higher plants and in some algae. Cellulose is widely used in the form of wood, agricultural fibres and paper products and in the form of cotton throughout the world. The basic structural repeating unit for cellulose is the cellobiose unit. The second ring in the cellobiose unit is chemically identical to the first ring. The important difference is that the second ring is inverted from the general plane of the first ring. The rings are not planar but puckered. Each ring is called an anhydroglucose unit. Since each one is identical chemically, it is more convenient to express cellulose as a polymer with the anhydroglucose unit as the repeating unit. Each unit contains three alcohol hydroxyls (—OH). These hydroxyls form hydrogen bonds inside the macromolecule itself (intra-molecular) and between other cellulose macromolecules (intermolecular). Cellulose is highly crystalline, regardless of source. The highly crystalline regions represent a tight packing of ordered chains wherein the hydrogen bonding is at a maximum. Cellulose also contains amorphous regions in which there can be a variation from complete disorder of the chains to some order.

10.2.2 Cotton

The origin, development, morphology, chemistry, purification and utilisation of cotton have been discussed by many authors.[3,4] Cotton is the most important textile fibre, as well as cellulosic textile fibre, in the world, despite inroads made into its markets by synthetic fibres. Worldwide, about 38% of the fibre consumed is cotton. The cotton plant grows naturally as a perennial, but for commercial purposes it is grown as an annual. Cotton fibres used in textile commerce are the dried cell walls of formerly living cells. Cotton is a unique textile fibre because of the inter-relationships of its subunits. Typically, cellulose in all the cell walls is in small crystalline microfibrils that are arranged in multilayer structures. However, only in the cotton fibre have so many organisation levels been discovered, and the special properties of cotton depend on this complexity. From its multicomponent primary wall, through the pure cellulose secondary wall to the lumen, the organisation of sub-fibre units provides the fibre with characteristic properties that make it a processable, strong and comfortable textile fibre. The cotton fibre is composed mostly of the long-chain carbohydrate molecule cellulose (the sugar of cell walls). Of all existing natural cellulose fibre sources, cotton cellulose is the purest. Raw cotton fibre, after ginning and mechanical cleaning, is essentially 95% cellulose. After treatments to remove the naturally occurring non-cellulosic materials, the cellulose content of the fibre is over 99%. The non-cellulosic constituents are nitrogen-containing compounds (proteins), wax, pectic substances (e.g. pectic acid, iron pectates, etc.), organic acids (malic and citric acids), sugars and ash-producing inorganic salts.[3]

10.2.3 Other vegetable fibres

In a broad sense, the source of vegetable fibres, as the name suggests, is the rich plant life of mother earth. In a narrower sense, different fibres come from different parts of different plants. A widely accepted classification of fibres is one that is based on their location in the plant. Accordingly, the three principal categories are seed fibres, bast fibres and leaf fibres. Those that do not fit into one of these three categories are lumped together as miscellaneous fibres. Vegetable fibres include sisal, jute, hemp, flax, ramie, etc.[5,6]

The chemical composition of vegetable fibres has attracted the attention of many investigators and it is generally agreed that the fibres contain one or more of the following:[7]

- Fats and waxes, mostly found on the surface
- Water solubles, extracted by boiling the dewaxed fibres in water
- Pectin, on the water-insoluble form of calcium, magnesium or iron salts of pectic acid.
- Hemicelluloses, which are amorphous short-chaine isotropic polysaccharides and polyuronides
- Cellulose, which is the principal constituent of the fibre ultimates

- Lignin, a short-chain isotropic made up of units derived from phenylpropane, which is found in the middle lamella of the fibre bundle.

Of the components listed above, the cellulose, hemicellulose and lignin are considered the three principal constituents. Most vegetable fibres also contain a proportion of acetyl groups that are readily hydrolysed by dilute alkali to acetic acid. Estimation of the quantity of acetic acid produced per unit weight of fibre then provides an index of the acetyl content. Most vegetable fibres are strong fibres but exhibit brittle fracture and have only a small extension at break. They have a high initial modulus, but show very little recoverable elasticity. Vegetable fibres are often used in handicraft industries, to make textiles, to make paper products, or to produce a variety of composites. The largest potential markets are in composite products. Vegetable fibre-based composites are often classified by their uses, e.g. geotextiles, filters, sorbents, structural composites, non-structural composites, moulded products, packaging, etc.[5]

10.2.4 Wood-pulp fibres

Fibres derived from wood-pulp are used in large quantities in the hygiene industry because of their absorbing properties. Wettability, absorption and liquid-holding capacity are important properties related to the physical nature of the capillary system and the chemical and physical nature of the exposed fibre surfaces, and these have to be optimised in order to meet the demands on the product The main natural fibre source worldwide comprises various softwood and hardwood species. Apart from small amounts of inorganic material, wood pulp fibres consist of carbohydrates (cellulose and hemicellulose), lignin and small amounts of organic low molecular weight material.[8]

10.2.5 Man-made cellulosics

There are different types of man-made cellulosics. Cellophane and viscose are probably the most well known and most frequently subjected to surface modification.

Cellophane was invented by Jacques E. Brandenberger, a Swiss textiles engineer, in 1908. Cellophane is a thin, transparent sheet made of processed cellulose. Cellulose fibres from wood or cotton are dissolved in alkali. This solution is extruded through a slit into an acid bath to reconvert the viscose into cellulose. A similar process, using a hole instead of a slit (a spinneret), is used to make a fibre called rayon.

Cellophane's low permeability to air, grease and bacteria makes it useful for food packaging. Cellulose film has been manufactured continuously since the mid-1930s and is still used today. As well as packaging a variety of food items, there are also industrial applications, such as a base for self-adhesive tapes such as Sellotape and Scotch Tape, a semi-permeable membrane in certain types of battery, and as a release agent in the manufacture of fibreglass and rubber products. Typically, however, the use of the word 'cellophane' has been genericised, and is often used informally to refer to a wide variety of plastic film products, even those not made of cellulose.[9]

Viscose is a regenerated cellulosic fibre, which is widely used in apparel, home furnishing and industrial materials.[10,11] Basically, all methods for producing rayon filaments or fibres depend on the solubilising of cellulose by alkali (aqueous sodium hydroxide), then reshaping it into long-fibred products by extrusion through the small holes of a spinnerette, immediately followed by conversion into solid cellulose. Although there are a number of ways in which this can be done, the viscose process is by far the most important and widely practised. The basic chemical unit of viscose is the anhydroglucose unit of the cellulose molecule. Viscose consists primarily of type II anti-parallel crystalline structure, rather than type I parallel crystalline structure in natural cellulosic fibres. Viscose has a much lower degree of polymerisation than cotton, and 40% crystallinity versus 60% for cotton.[12,13] Viscose is mainly based on wood pulp fibres and cotton.

Chemically modified regenerated celluloses can be spun, moulded and cast into films. Examples of these are cellulose acetate fibres, which have high luster and sheen and are frequently utilised in garment linings, and cellulose acetate films, which find applications ranging from photography and sausage casings to dialysis membranes. Cellulose acetate butyrate and cellulose acetate propionate can be used to make strong, resistant, plastic tool handles.[1]

10.3 Mechanisms of interactions between plasmas and cellulose-based fibres

Cellulose, as have all polysaccharides, has traditionally been modified through reactions of the hydroxyl group, the only functional group generally available for reaction. This has generally limited the reactions to esterification and etherification. The hydroxyl groups on the anhydrosugar units vary in reactivity and, with polyglucans for example, the C6 hydroxyl is favoured in esterification and the C3 is favoured in etherification reactions. It has also been demonstrated that the accessibility of the OH groups is controlled by the relative ratios of crystalline and amorphous regions of the cellulose suprastructure. The hydroxyl reactivity can be quantified by exposure to TFAA (trifluoroacetic anhydride) vapour followed by XPS analysis. The ease with which a hydroxyl centre can be derivatised was found to be directly dependent upon its crystallinity. Amorphous celluloses can be functionalised much more readily than their crystalline counterparts.[14]

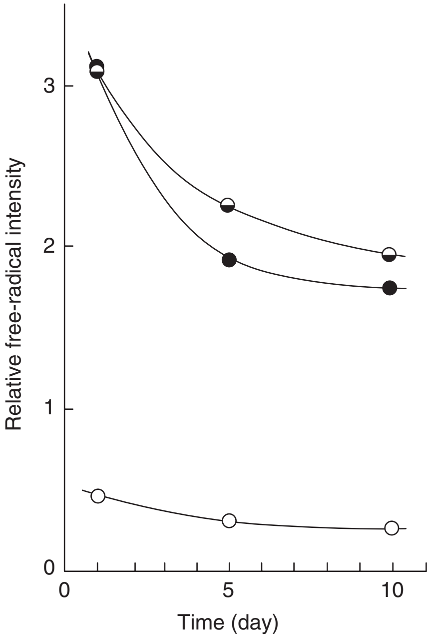
The use of cold plasma is a new approach to cellulose modification, varying significantly from the traditional esterification and etherification routes. Plasma gas substituents can be reacted directly with the anhydrosugar units by abstraction of hydrogens from either carbon or oxygen atoms in the plasma reactor. Thus, cellulose can be oxidised, reduced and/or substituted in new, unique ways. Cellulose can also be grafted with vinyl monomers by using the plasma as a free-radical initiator at the cellulose surface. Because the monomer is introduced as a gas, no wasted homopolymer is formed and the grafting is restricted to the surface.[1]

10.3.1 Free radical formation and stability at cellulose surfaces

The interaction of the active species of a plasma with cellulose (and other polymer) surfaces, involves several electron-mediated processes, as well as positive ion-induced reactions. Some of these reactions can promote homolytic bond cleavages leading to the formation of free-radical sites. These reactive centres can lead to a variety of functionalisation mechanisms, depending on where in the cellulose structure they are created. Free radical sites usually contain unpaired electrons which are not involved in chemical bonding, and this determines their extremely high instability and high reactivity. As a consequence, free radicals generated on a polymer surface, e.g. as a result of the interaction with a plasma in a closed vacuum environment, and which are subsequently exposed to atmospheric conditions, disappear almost instantaneously through water vapour or moisture-driven recombination mechanisms, which make their identification and detection very difficult. However, some of these free radicals can be quite stable below the surface layers of the substrates through sterical hindrance and 'caging' effects. It is possible to investigate these active species, both by chemical (e.g. reaction with sulphur dioxide or diphenylpycryl-hydrazil) and physical (electron spin resonance (ESR)) techniques.[1]

ESR measurements indicate that significant free radical concentrations can be created on polymeric surfaces under cold plasma environments, regardless of the nature of the substrates or plasma gases.[14] Argon, O_2, N_2, H_2, CO, CH_4 and CF_4 plasma-generated relative free-radical intensities from cellulose fibre surfaces such as cotton, linen, viscose rayon and polynosic fibres, and from wool, silk, nylon 6 and poly(ethylene terephthalate) have been measured by the ESR technique. It was shown that trapped free radicals can survive in the polymer matrix and that their intensities vary significantly with the nature of the fibres and the plasma gases. The following order of free-radical intensities was established for various substrates and plasma gases: cotton > linen > mercerised cotton > nylon 6 > polynosic fibres = viscose rayon, and $CF_4 > CO > H_2 > Ar > CH_4 > N_2 = O_2$. It was also found that longer treatment times induce higher free-radical concentrations. In addition to the plasma parameters, the fine structure of the fibres plays an important role in the generation and stability of plasma-created free radicals. It has also been concluded that there is no direct relation between free-radical intensity and the extent of surface modification. XPS evaluation of the relative surface atomic compositions of CF_4 plasma-treated cellulosic fibres demonstrated that exposure to the CF_4 discharge induces similar surface chemistry (i.e. comparable relative surface atomic compositions) regardless of the nature of the substrate. However, the free-radical intensities of natural and regenerated cellulose fibres differ significantly.

The stability of living free radicals 'trapped' in cotton fibres after exposure to O_2, CF_4, and CO plasmas at different temperatures has been investigated under open laboratory conditions, see Figure 10.1. The activated fibres were conditioned at room temperature, as well as in a temperature range of 120–200°C. It was shown that the relative free-radical intensities



10.1 Stability of free radicals generated on cotton by O_2, CO, and CF_4 plasmas in air at room temperature. (Reproduced with permission from Ref. 15.)

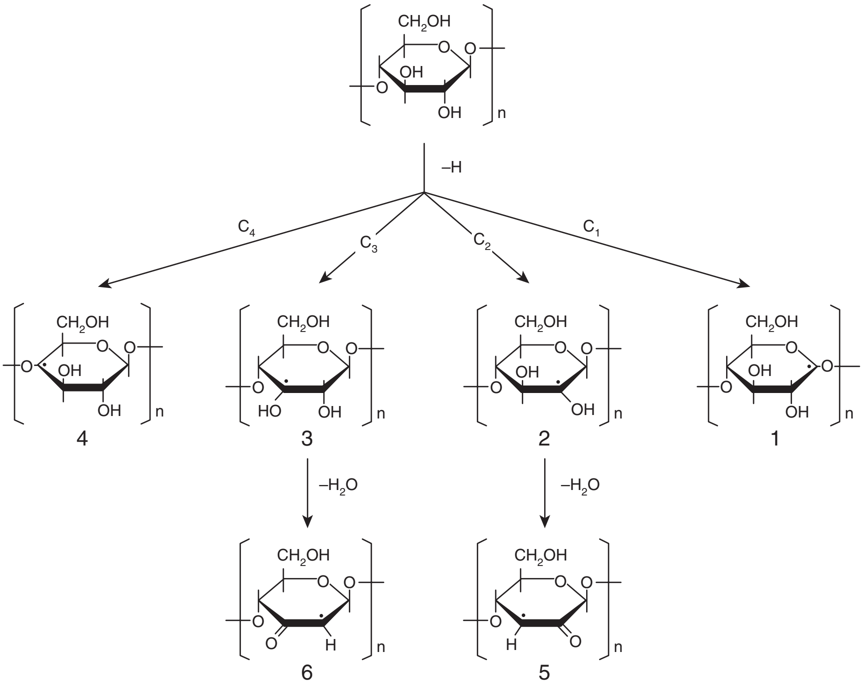
of the CF_4 and CO plasma-treated fibres decreased markedly with an increase in temperature and exposure time to air, whereas free-radical intensities of oxygen plasma-treated substrates did not undergo substantial changes. Similar free-radical instabilities have been observed on argon plasma-treated jute and cellulose.[16] Tests with non-extracted and plasma-treated jute and plasma-exposed ethanol-extracted lignin indicate that the lignin plays a significant role in the free-radical formation, and that the low-molecular weight extractives inhibit the free-radical formation.

Detailed and systematic evaluation of the nature and intensity of free radicals generated on polysaccharides, by coupling ESR kinetics with computer simulation, allowed identification of the precise nature of the plasma-created free-radical sites.[17] It was demonstrated that all possible four hydroxyalkyl radicals (1, 2, 3, and 7) are generated as primary structures through the hydrogen abstraction mechanism, but with a preference at C2 and C5 carbon atoms. The radicals formed at C4 and equivalent C6 were unstable, i.e. they underwent spontaneous thermal dehydrogenation resulting in acylalkyl radicals, whereas radical C1 was stable even at temperatures as high as 120°C.[18]

An in-depth ESR study of Ar plasma-induced polycarbohydrate radicals in powdered cellulose and amylose demonstrated a significant difference between the ESR spectra from the two anomeric polymers.[19] The spectra of the plasma-exposed cellulose contained a large amount of an isotropic triplet (*ca* 2.8 mT hyperfine splitting constant (HSC)) in addition to the doublet, whereas plasma-irradiated amylose contained only a negligible amount of the triplet. This triplet is assignable to the hydroxylalkyl radical C2 and/or C3 of the glucose units of cellulose. The lack of triplet formation in the amylose was considered due to the suppression of hydrogen abstraction at C3 in the helical tertiary structure of amylose. It was also shown that the polycarbohydrate radicals react rapidly with oxygen under open laboratory conditions, whereas monocarbohydrate radicals are stable even at elevated temperatures. This difference was ascribed the difference in the polymorphic forms between poly- and monocarbohydrates.[19] The structure of the plasma-induced radicals in cellulose and the reaction sequence are illustrated in Figure 10.2.

10.3.2 Generation of high surface energy cellulose substrates – Ar and O_2 plasma treatments

Surface functionalisation of natural polymeric substrate surfaces from non-polymer forming plasmas (inert- and reactive-gas plasmas) are of special interest in theoretical and applied investigations for the following reasons:



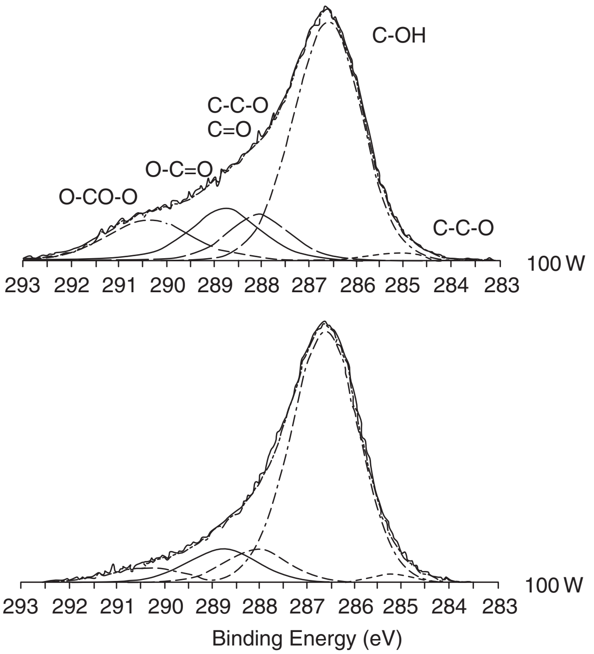
10.2 Structure of plasma-induced radicals in cellulose, and the reaction sequence. (Reproduced with permission from Ref. 18.)

- These processes are by-product free. The reactions are not accompanied by the deposition on the substrate or reactor wall surfaces of undesired macromolecular layers. Small quantities of gas phase components from ablation mechanisms or from plasma-induced molecular dissociation reactions usually do not create significant environmental problems.
- The plasma installations do not require periodic difficult cleaning procedures, which make this approach suitable for continuous-flow systems.
- The starting components usually are volatile, low molecular weight gases which can easily be fed into the reaction chamber.

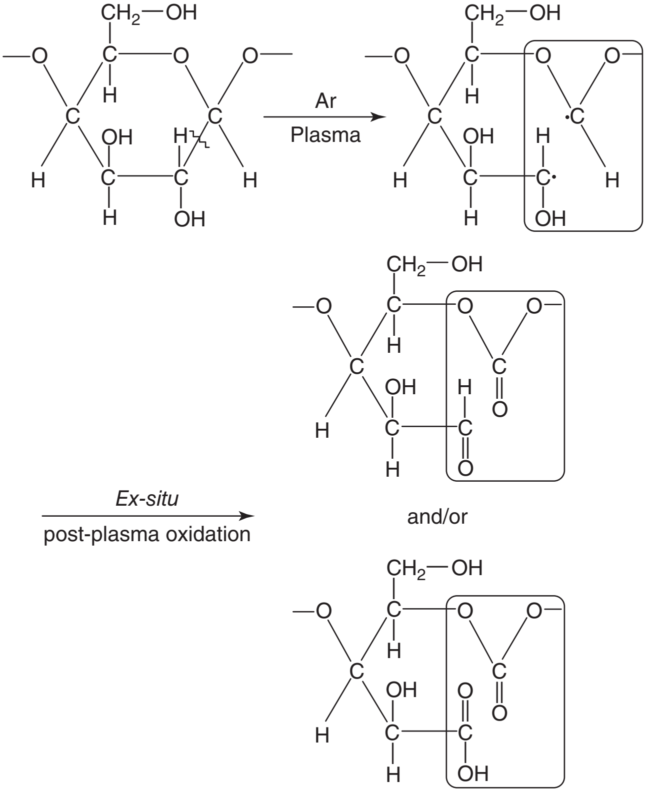
The approach of Ar and O_2 plasma treatments is generally directed to create polar functionalities other than hydroxyl groups on the cellulose surfaces.

Argon plasma-treated cellulose surfaces

Several studies of O_2 and Ar plasma treatments of Whatman filter paper indicate that identical surface functionalities are created but through different reaction mechanisms. Relative percentage surface areas of non-equivalent carbon peaks of high resolution XPS data collected from argon plasma-treated samples, indicate that new surface functionalities are formed compared with unmodified cellulose. In addition to the C—OH, C—O—C (286.6 eV) cellulose peaks, the existence of O═C═O (288.7 eV) and O—CO—O (290.4 eV) binding energy can also be noticed. Plasma-induced surface modification at higher RF powers involves mainly the diminution of the O—C—O linkages of the pyranosidic unit through the cleavage of the C1–C2 bonds. The formation of ketone and aldehyde functionalities as a result of the ring opening process, demonstrated by high resolution XPS data from Ar-plasma-treated samples, substantiate the suggested reaction mechanisms (see Figure 10.3). The oxidation processes of Ar plasma-treated cellulose are related to plasma-created free radicals, which initiate post-plasma oxidation reactions under open laboratory conditions.[20,21] The suggested reaction mechanism for argon plasma-induced molecular fragmentation of cellulose is shown in Figure 10.4.



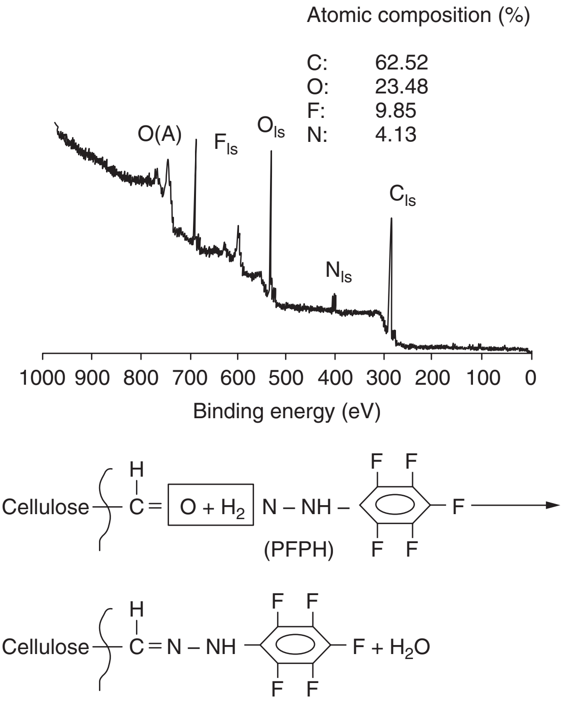
10.3 High resolution deconvoluted XPS spectra of cellulose (Whatman paper) treated at 100 and 500 W under argon-RF-plasma conditions. (Reproduced with permission from Ref. 21.)



10.4 Suggested reaction mechanism for argon plasma-induced molecular fragmentation of cellulose. (Reproduced with permission from Ref. 21.)

Oxygen plasma-treated cellulose surfaces

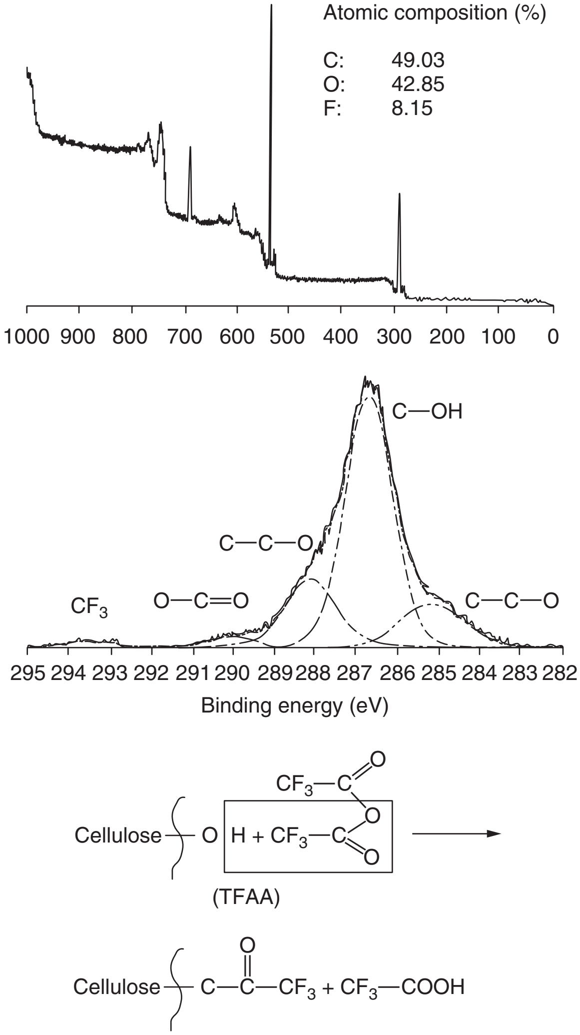
Similarly to the Ar plasma-modified cellulose, XPS data collected from O_2 plasma-modified and PFPH-(pentafluorophenylhydrazine) and TFAA-(trifluoroacetic anhydride)-derivatised cellulose substrates clearly indicate the presence of O—C—O in all plasma-modified samples, but also formation of new O═C—O, C═O and O—CO—O functionalities. However, in this case C—OH and C—O—C linkages are involved in plasma-induced reaction mechanisms. It has been suggested that the relative increase of O—C—O concentration is related to the diminution of C—OH and C—O—C concentrations. The intensified reaction mechanisms involving C—OH and C—O—C groups at higher pressure values were suggested to be associated with cross-linking mechanisms. High resolution XPS data from PFPH-derivatised samples also indicate the presence of C═O functionalities.[21] The suggested mechanisms for the reactions of PFPH and TFAA



10.5 Survey ESCA spectrum of a typical argon plasma-treated and pentafluorophenyl hydrazine-derivatised cellulose substrate and the derivatisation reaction mechanism. (Reproduced with permission from Ref. 21.)

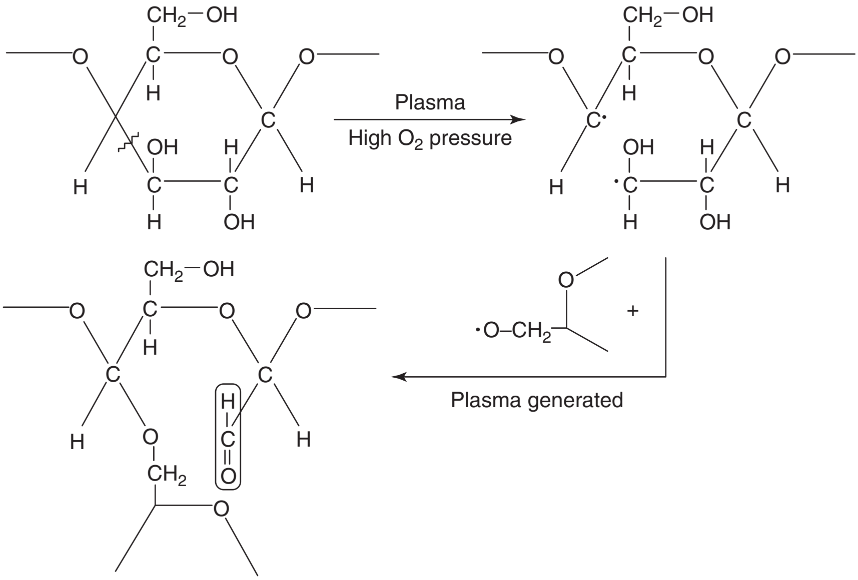
with both C═O and C—OH functionalities are illustrated in Figures 10.5 and 10.6, respectively.

ATR-FTIR analysis of O_2 plasma-treated cellulose correlates well with the XPS data. A typical IR spectrum of virgin cellulose shows all the typical characteristic vibrations: OH wagging at $670\,cm^{-1}$; C1 group vibration, C—C stretching, C—C—O stretching, C—O—C symmetric stretching, and CH_2 bending at 893, 1000, 1060, 1120 and $1370\,cm^{-1}$, respectively; in-plane OH bending at $1400\,cm^{-1}$; CO_2 at $2359\,cm^{-1}$; C—H stretching at $2900\,cm^{-1}$; OH and intermolecularly bonded OH at $3100–3400\,cm^{-1}$ and water at $3742\,cm^{-1}$. O_2 plasma-treated cellulose substrates show more intense in-plane OH vibrations (at $1390–1420\,cm^{-1}$) and the presence of weak unsaturation absorption (at $1600\,cm^{-1}$) in comparison with the spectrum of untreated cellulose. Analyses of TFAA-derivatised versions of untreated and O_2 plasma-treated cellulose show that the in-plane OH vibrations at 1390–$1420\,cm^{-1}$ disappear almost totally and the C═O vibrations of aryl esters appear at $1640–1680\,cm^{-1}$ upon plasma exposure. The ATR-FTIR data support the XPS data and indicate that macromolecular chain-breaking



10.6 Survey ESCA spectrum of a typical argon plasma-treated trifluoroacetic anhydride-derivatised cellulose substrate and the derivatisation reaction mechanism. (Reproduced with permission from Ref. 21.)

mechanisms and plasma-induced etching processes control the number and availability of OH functionalities at the surface of the plasma-modified samples. In other words, the O_2 plasma treatment seems to cause more intense C—O—C scission reactions on the cellulose surface. The suggested cross-linking mechanism for O_2 plasma-exposed cellulose is shown in Figure 10.7.[21]



10.7 Suggested cross-linking mechanism for O_2 plasma-exposed cellulose. (Reproduced with permission from Ref. 21.)

10.4 Plasma modification of cotton for textile applications

The textile industry has long been concerned about water consumption and environmentally hazardous chemicals in effluents.[22] The method used to graft monomers onto cellulosic fabric, for instance was, for many years, based on the use of initiators (such as ceric ions) for copolymerisation between cellulose and the monomer. The main drawback of this method is the generation of highly toxic wastes.[23] In recent years, low-temperature plasma technology for surface modification of textile substrates has attracted increasing attention. It has been established that plasma treatment plays a key role in the enhancement of textile fibres and fabrics properties, such as improved wettability, dyeing, water repellency, lowered moisture content, and decreased surface resistivity.[24] Several studies on plasma surface modification of cellulose-based textiles have been conducted, using glow-discharge technology at low pressure[22–40] as well as barrier discharge and corona treatments at atmospheric pressure.[41–50] In both cases, active particles such as radicals, ions, electrons and photons are generated, which under reduced pressure have a much larger free path length as compared with the process at atmospheric pressure. Consequently, the treatment at atmospheric pressure normally occurs in a narrow slit, while the treatment at low pressure is performed in a reactor with a volume adapted to the size of the samples.

10.4.1 Plasma surface modifications of cotton at low pressure

Air and oxygen plasma treatments of cotton fibres were studied under variation of the most important plasma parameters, such as discharge power, treatment time and nature and flow rate of the gas. The chemical effect of the treatments on the cotton fibres was evaluated by means of a variety of different methods, including the Cuprammonium fluidity test, weight loss measurement, determination of carboxyl groups, carbonyl group identification, FTIR analysis and ASTM yellowness. In addition, vertical wicking, the effect of ageing of the plasma treatments and amount of dye uptake were investigated. It was found that the plasma treatments led to surface erosion of the cotton fibres, which generated a weight loss, accompanied by an increase in the fibre carboxyl group and carbonyl group contents. The increase in carboxyl group concentration led to a more wettable fibre and the rate of fabric vertical wicking was increased. The direct dye (chloramine Fast Red K) uptake increased almost linearly with the increase in fibre carboxyl group content, but decreased progressively with increased ageing time after the oxygen plasma treatment. It was also shown that the fabric yellowness increased with time after treatment.[33]

Several attempts have been made to introduce different functionalities/properties to the cotton fibre surface by means of plasma-induced graft polymerisation. Often hydrophilic monomers have been polymerised on the cotton surface, previously activated by, e.g. an inert-gas plasma, in order to improve the mechanical properties of the cotton.[37] The most commonly used hydrophilic monomers are various methacrylates and acrylates (e.g. HEMA (2-hydroxyethyl methacrylate), GMA (glycidylmethacrylate), MEA (2-methoxyethyl acrylate), HEA (2-hydroxyethyl acrylate)) and other vinyl monomers such as acrylic acid acrylamide, N-isopropyl acrylamide, etc.

A variety of these hydrophilic monomers were grafted onto cotton and other textile fibres that had been pre-treated by glow discharge plasmas. A piece of textile fabric was exposed to an argon plasma generated at 13.56 MHz frequency. Previously degassed monomer solutions were then poured into the reactor without contact with air. The graft polymerisations were thus carried out in an aqueous phase under shaking in a water bath at a controlled temperature (60–65 °C) for 2 hours. It was found that HEMA was graft-polymerised more readily than the other monomers investigated. The grafting yield decreased with increasing air-exposure time and it was concluded that vacuum processing is crucial for successful graft polymerisation. The mechanical properties, in terms of breaking strength, of the poly(HEMA)-grafted cotton yarns were improved. The increase in breaking strength was attributed to the binding of fibrils in the yarn by the graft polymer. The Ar plasma treatments alone caused a reduction in strength due to etching.[37]

Low temperature plasma was used to activate mercerized cotton fabrics, to be followed by grafting of various methacrylates.[51] Preliminary trials using glycidylmethacrylate (GMA) onto plasma-treated cotton fibres were carried out to select the most suitable gas and plasma conditions in order to obtain the highest possible graft yield of GMA. Argon was found the most efficient gas with respect to induced graft yield. ESR was used to study the formation of the different radical species generated on the plasma-treated cellulose of mercerised cotton substrate. The ESR results were in accordance with the graft yield results and showed proportionality between the total concentration of radical species and applied discharge power. The suggested reaction mechanism of surface-initiated free-radical polymerisation consists of an initiation step involving primary radicals generated directly by action of the Ar plasma on the cotton substrate, or indirectly by action of peroxides formed by interaction between radicals and atmospheric oxygen.[51]

It is also possible to graft hydrophobic, water-repellent functionalities onto the cotton fibres.[22,26,37] Radiofrequency-driven plasma processes are the most commonly used processes for textile substrate modification. However, the use of 2.45 GHz microwave generator plasma for surface modification of cotton fabrics has also been reported. One study demonstrated that an argon plasma at 2.45 GHz generated more active groups on cotton than either N_2 or O_2 plasma treatments.[51] It was also reported that vinyl laurate was successfully plasma-induced grafted onto lightweight cotton fabric, thereby imparting a hydrophobic character to the fabric surface.[52] Another study investigated the effect of microwave plasma treatment on fabric weight loss and breaking strength and the durability to repeated home laundering of the plasma-induced grafting of vinyl laurate on the fabric. Microwave plasmas using O_2, N_2 and argon, at various discharge powers and exposure times, were applied to the lightweight cotton fabric. The results showed that O_2 plasma generated higher weight loss than N_2 and Ar plasmas. The fabric breaking strength was not affected by the microwave power or by the type of plasma. However, longer exposure time to plasma may result in significant strength loss due to excessive etching and depolymerisation. Plasma-induced grafting of vinyl laurate monomer onto the fabric surface resulted in stable cellulose–vinyl laurate copolymers. Water contact angle measurements after repeated home laundering did not show any significant effect on the water repellence of the grafted cotton fabric. The fabric strength losses due to the plasma treatments were only a fraction of the losses experienced with traditional textile finishing resin.[24]

Besides plasma activation with non-polymerisable gases and plasma-induced grafting of various monomers, it is also possible to modify cotton surfaces by means of plasma polymerisation, i.e. deposition of ultra-thin layers directly from the gas phase in the plasma.[26,27] The character of the deposited layer depends on the precursor (monomer) and can be anything from very hydrophilic to very hydrophobic.

Plasma polymerisation of dichloromethane (DCM) was found to be extremely effective with respect to improving properties such as moisture content and dyeability of cotton fabrics.[26] However, at polymerisation times beyond 20 seconds, an adverse effect was seen: the moisture content decreased along with colour strength. The decrease in moisture content showed a hydrophobic behaviour of the cotton fabric with a consequent effect on the dyeability of the modified fabric. An increase of yellowness in the plasma-coated cotton sample with increasing deposition time of DCM was also observed. The other properties remained unchanged. It was suggested that increased generation and deposition of free radicals of both plasma and DCM vapour onto the cotton surface with increased deposition time, were the causes of the yellowness of the surface.[26]

Several studies have shown that exposure of the cotton fibres to fluorinated gas plasmas results in a decrease of water absorption or wettability.[22,25,53] Fluorocarbon gas plasmas can change surface properties via either surface treatment or polymerisation and deposition of a thin film.[22,53–55] Cotton fabrics were treated by RF plasma with tetrafluoromethane (CF_4) and hexafluoropropylene (C_3F_6) gases at different plasma conditions[22] in order to make the fabric surface hydrophobic. The hydrophobicity and water repellence were determined by measurements of the cosine of the contact angle ($\cos \theta$) and wet-out time. The hydrophobicity was enhanced with treatments by either gas but XPS analyses revealed a significantly higher fluorine content on the cotton surface after the C_3F_6 plasma compared with after the CF_4 plasma treatment. It was also found that the increase in contact angle and wet-out time achieved by C_3F_6 plasma treatment were substantially higher than those after treatments in CF_4 gas plasma. These differences were mainly due to the fact that C_3F_6 plasma can generate polymers on the substrate through both plasma polymerisation and plasma-induced polymerisation mechanisms, whereas CF_4 gas plasma is limited to only plasma polymerisation. In addition, CF_4 plasmas produce more atomic fluorine than C_3F_6 plasmas, and it is well known that CF_4 is a highly effective etchant and ablates the deposited fluorinated polymer layer. This results in a reduction in surface fluorine and a decrease in hydrophobicity over time. Using C_3F_6 plasma to make cotton fibres and other surfaces hydrophobic therefore appears to be the preferred choice over CF_4 plasma.[22]

10.4.2 Plasma surface modifications of cotton at atmospheric pressure

Despite the high efficiency of low-pressure plasma treatments, the wide use of vacuum-based plasma technologies has been discouraged by high investment costs, batch-wise processing and relatively long treatment times (on the order of minutes). The basic advantages of atmospheric-pressure plasma processing consist of comparatively simple implementation, no need for maintaining vacuum and possibility to organise the process based on continuous technology. A more extensive description of atmospheric-pressure plasma processes is given in Chapter 4 of this book ('Atmospheric-pressure cold plasma processing technology').

The first studies on corona treatment[56] (the first and most simple form of atmospheric pressure plasma) of cotton were reported at the beginning of the 1960s.[42] Corona treatment of cotton and its effect on spinnability, strength, abrasion resistance, friction properties, etc., have been investigated by several research teams.[41,43–45] It was found that corona treatments increased yarn strength (particularly for soft twisted yarns) by modifying the fibre surfaces to increase friction between fibres. It was demonstrated that the properties of the cotton fibre surface were permanently modified without any change in fibre strength.[45] It has also been demonstrated that the cohesion of twistless cotton slivers can be increased substantially by continuous corona-discharge treatment. It was also claimed that the most efficient method for a given total power input is to use multiple treatments at a number of separated treatment points rather than to rely on a single treatment in a single, concentrated corona field.[41]

In more recent years, other, more sophisticated, atmospheric pressure plasma processes (e.g. various dielectric barrier discharges,[50,57–60] have been developed. Cotton yarn was treated with an airflow-stabilised DC (direct current) discharge in the glow regime. It was demonstrated that the wicking rate of the treated cotton yarn increases with treatment time and discharge power. It was also indicated that the wicking rate was higher when the yarn was positioned in the vicinity of the electrodes. Some ageing of the treatment, i.e. decrease in wicking rate, was observed during the first 5 hours, but the decrease levelled off and the remaining wicking rate was significantly higher than the wicking rate for the untreated yarn.[50]

10.5 Plasma surface modification in cellulosic fibre-based composites

To create composites of polysaccharide and thermoplastic-based materials, at least one of the two dissimilar materials should be modified to make it compatible with the other. It has been shown that cold plasma environments are suitable for tailoring surface characteristics of cellulosic substrates and for increasing adhesion with their synthetic counterparts.[61–63] However, surface treatments of thermoplastics were also found to be effective in creating composites.[64] Results from hydrogen and oxygen RF-plasma treatments of filter paper (open texture and free from low-molecular-weight materials) and grease-proof paper (closed texture and the presence of low-molecular-weight compounds) indicated that hydrogen plasma environments reduce the cellulose surfaces and generate low molecular weight degradation products, whereas oxygen plasma exposure increases the relative surface oxygen content and improves adhesion (see Figure 10).[61] It was shown that reduction of cellulose surfaces does not influence the adhesion significantly. However, the presence of degradation products strongly diminishes this characteristic. The increased adhesion of oxygen plasma-treated cellulosic substrates to polyethylene is related to the ablation of low molecular weight components (resins in the case of greaseproof paper) and to the formation of hydroperoxide-mediated covalent bonds across the interface. It was also shown that the lamination temperature of the cellulose/thermoplastic composites significantly influences the adhesive strength only in the case of the filter paper.

Wood fibres from 60% beech and 40% birch, containing 86% cellulose, 13% hemicellulose, and a very small fraction of lignin, were treated in different microwave discharges.[63] By controlling the plasma environment, the acid/base interaction balance can be shifted towards acidity or basicity. Acidic character of the fibres was achieved by plasma polymerisation of methyl methacrylate, and the basic character was obtained by ammonia and nitrogen plasma treatments. It was emphasised that the surface treatments were incomplete, although the plasma reactor used was provided with a fibre-mixing system. It was shown that the mechanical properties of composites from plasma-modified cellulose fibres and polystyrene and chlorinated polyethylene were improved when a strong acid–base interaction between the matrix and the fibres was favoured. The properties of PP-based composites were not affected by the acid–base characteristics.

The effect of plasma treatments on the mechanical properties of composites made up from cellulosic fibres, in particular sisal fibres, and thermoplastics such as polypropylene and polyethylene, has been investigated by several authors.[65–73] Most studies showed that air and argon plasma treatments improved the compatibility between sisal fibres and polypropylene.

Both treatments, and air plasma in particular, improved the mechanical properties of the resulting composites in terms of strengths and moduli in both tensile and flexural modes. However, it was demonstrated that the plasma conditions are very critical. Optimised plasma treatment parameters were found at short (≤30 seconds) treatment times, and medium power and medium chamber pressures. Dynamic Mechanical Thermal Analysis (DMTA) showed that the storage modulus of the plasma-treated sisal fibre–PP composites improved over the whole temperature range (–60 to +160 °C), indicating better adhesion between the sisal fibre and the PP matrix. In particular, the interfacial shear strength increased more than 20% after an air plasma treatment for 30 seconds. Longer treatment times resulted in a significant reduction in interfacial shear strength. Surface characterisation by XPS showed that the O/C ratios of the sisal fibres increased after both Ar and air plasma treatments. The air plasma treatment yielded higher O/C ratios than Ar plasma. It was proposed that this higher O/C ratio, plasma-generated surface C=O and O—C=O functionalities, and selective etching of the surface by plasma, all contribute to better adhesion characteristics, which in turn results in better composite performance.[69,70] SEM analyses revealed that obvious corrugations and granules developed on the surface of the Ar plasma-treated fibres, and a number of cracks and an amount of scouring appeared on the fibre surface at prolonged air plasma treatment times. It has also been demonstrated that the plasma discharge frequency has a pronounced impact on plasma-induced degradation and chain scission in both polypropylene and sisal fibres during oxygen plasma treatments. Results showed that polypropylene–cellulose adhesion forces are about an order of magnitude higher for treatments at 13.56 MHz than at 40 kHz, owing to a much higher degree of chain scission at lower frequencies. Sisal fibres and PP powder treated in conditions of surface degradation did not improve in flexural or tensile properties but had higher impact resistance, comparable to the improvement obtained with the addition of compatibiliser.[66]

Sisal fibres and finely powdered high-density polyethylene (HDPE) were surface-functionalised with dichlorosilane in a RF-plasma reactor and the mechanical properties of composites made from the plasma-treated materials were investigated. In contrast to other studies, it was found that the best mechanical performance generally was obtained for composites where only the thermoplastic matrix (HDPE) was plasma-functionalised, which led to good interfacial adhesion between fibres and matrix. Plasma treatment of lignocellulosic fibres induced decomposition processes of the surface layer structures exposed to the plasma, which generally does not contribute to significant improvement of the mechanical behaviour of the composite. It was therefore suggested that only the thermoplastic substrate should be plasma-functionalised.[67,68]

Attempts have also been made to improve the compatibility and adhesion to polypropylene by making the cellulose fibre surface polypropylene-like.[72] Cellulose filter paper was treated with cyclohexane plasma under various conditions to evaluate this approach. Plasma polymerisation of cyclohexane is known to produce hydrocarbon-type polymer coatings. ESCA (XPS), dynamic contact angle measurements and SEM analysis were used to determine the nature of the chemical changes on the plasma-coated cellulose surfaces. The cyclohexane plasma treatments resulted in the deposition of an oxidised and dehydrogenated hydrophobic polymer film, similar in structure to polyethylene. Although compatibility with polypropylene was improved by covering the polar groups on the cellulose surface with non-polar plasma-generated polymer materials, adhesion was not at all improved. A cyclohexane plasma may increase the compatibility and intimate molecular contact between polypropylene and filter paper, but the lack of hydrogen and/or covalent bonding results in no strength development in the laminated structures.[72]

Various wood fibres (e.g. high temperature mechanical pulp (HTMP) and high alpha hardwood) have also been plasma-treated in order to improve their adhesion to thermoplastics, and mechanical properties of the resulting composites.[71,74,75] Also, here, air and argon plasma treatments improve the tensile strengths and moduli of woodfibre–polypropylene composites. It was shown that the best result was obtained when both the wood fibre and the PP surface were treated. It was suggested that dispersive forces are mainly responsible for the increased interfacial adhesion.[71] Atomic Force Microscopy (AFM) analyses revealed that oxygen plasma treatment caused changes in the morphology of the materials. The treated PP surface was covered by a nodular structure, which was not seen on the untreated film. Similar nodular structures have also been observed after corona treatment of PP films.[76] These structures were also detected on the lignocellulosic material. The diameter of the nodules increased with increasing treatment time. The nodules seemed to have poor interaction with the PP surface, resulting in a weak interface between the plastic film and the wood. Consequently, the maximum adhesion was reached with the shortest plasma exposure time applied.[75]

Lately, some studies have reported on chemical modification of cellulose fibres for improvement of their interaction with rubber matrices. Allyl acrylate and allyl methacrylate were grafted on short cellulose fibres, resulting in improved wetting and increased adhesion to a natural rubber (NR) matrix.[77] Butadiene and divinylbenzene were plasma-grafted onto kraft pulp cellulose fibres in order to improve the mechanical properties of natural rubber–cellulose fibre composites. There was no difference in apparent cross-link density but the initial modulus was increased more than 150%. This effect was attributed to an increased adhesion/dispersion as a result of the plasma treatment.[78] Corona-treated wood flour was evaluated as a filler for nitrile butadiene rubber (NBR) compounds. The mechanical properties were investigated and it was found that corona treatment at optimal conditions improved these properties. The effect increased with increasing treatment time and discharge voltage. The improvement of the mechanical properties was explained by changes in the geometric area of the wood flour particles, caused by surface etching of the corona treatment, and the accumulation of surface oxygen-containing groups that changed the surface polarity of the wood flour particles.[79]

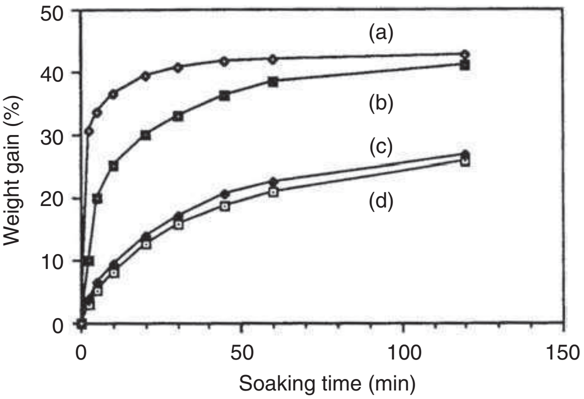
10.6 Plasma modification of solid wood and wood pulp fibres

10.6.1 Plasma modification of solid wood surfaces

Wood is a heterogeneous material consisting of two major components, carbohydrates and lignin, and minor components in the form of organic extractives and inorganic minerals.[80] Wood is a popular construction material due to its high physical strength, easy machinability, aesthetic appeal and low price. At the same time, wood has several disadvantages, such as biodegradability, dimensional instability with varying moisture content, significant reduction in physical strength at high moisture content and degradability by UV light, acids and bases.[81,82] Since most of these undesired properties are closely related to the hygroscopic nature of wood, reduction of water penetration into the pores is vitally important, especially when wood is exposed to outdoor environments. Lacquering, painting or oil impregnation are the most commonly used surface protection methods in order to ensure the retention of surface properties of wood in outdoor applications. The performance of these coatings is strongly influenced by the presence of liquid water since it can penetrate into the interface between the wood substrate and the coating and reduce the bond strength (wet adhesion) between the coating and the wood. This is especially critical for water-borne acrylic dispersions, where the wet adhesion occasionally is so critical that blistering, adhesive failure and other damages often occur.[83]

Low-temperature plasma technology offers, in principle, two routes to improved outdoor performance of wood: (i) plasma deposition of highly cross-linked hydrophobic coatings directly on the wood surface in order to prevent penetration of water into the wood pores,[84–88] and (ii) plasma cleaning and activation of the wood surface for improved adhesion of various protective coatings.[85,89–92] A few examples of each approach are given below.

Plasma-induced hydrophobisation of wood surfaces has been investigated to improve dimensional stability and biodegradability.[84] Pine sapwood samples were coated in a tubular RF-plasma reactor under methane (CH_4), tetrafluoroethylene (C_2F_4) and hexamethyldisiloxane (HMDSO) discharge environments. It was found that, due to the released water vapour and/or low-molecular-weight components from the wood under low pressure, the efficiency of plasma treatment was dependent on the evacuation time; that is, longer evacuation times resulted in more efficient treatments (see Figure 10.8). The nature of the plasma gases also influences the water uptake. C_2F_4 plasmas reduce the water uptake more than CH_4 and HMDSO plasmas after long evacuation, whereas at short evacuation times, HMDSO depositions result in the lowest water uptake values. The hydrophobised wood surfaces exhibited poor adhesion to paint. This characteristic could be improved through post-hydrophilic treatments, such as oxygen plasma treatment and plasma polymerisation of acrylic acid. The adhesion was improved at the sacrifice of the reduction of water uptake. However, a large reduction in water uptake and good adhesion to the paint could be achieved by a proper combination of the hydrophobic treatment and the hydrophilic post-treatment.[84] In another study, defect-free pine blocks were coated with plasma polymer films from vinyl acetate vapour, ethylene, acetylene and 1-butene. The plasma polymerisation proved to be a very promising technique to change the hydrophilic characteristics of wood surfaces without changing the bulk properties. The best hydrophobic effect was obtained by plasma polymerisation of 1-butene. However, the plasma-deposited film was



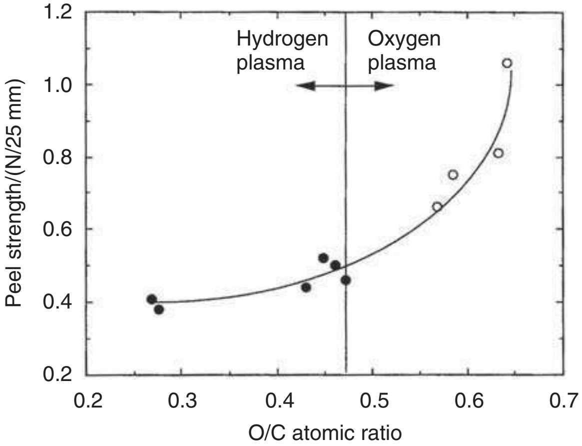
10.8 Weight gain in water of pine sapwoods (50 × 10 × 2 mm) treated with C_2F_4 plasma (5 sccm, 10 W, 10 minutes) as a function of soaking time. The plasma treatment is carried out at different evacuation pressures with corresponding evacuation time in parenthesis: (a) untreated sample, (b) 33 mTorr (5 minutes), (c) 18 mTorr (10 minutes), (d) 12 mTorr (30 minutes). The advancing water contact angles are for sample (a) 15°, (b) 94°, (c) 111° and (d) 128°. (Reproduced with permission from Ref. 84.)

unable to prevent absorption and desorption of water vapour since, it was concluded, the plasma technique was unable to coat wood capillaries.[86]

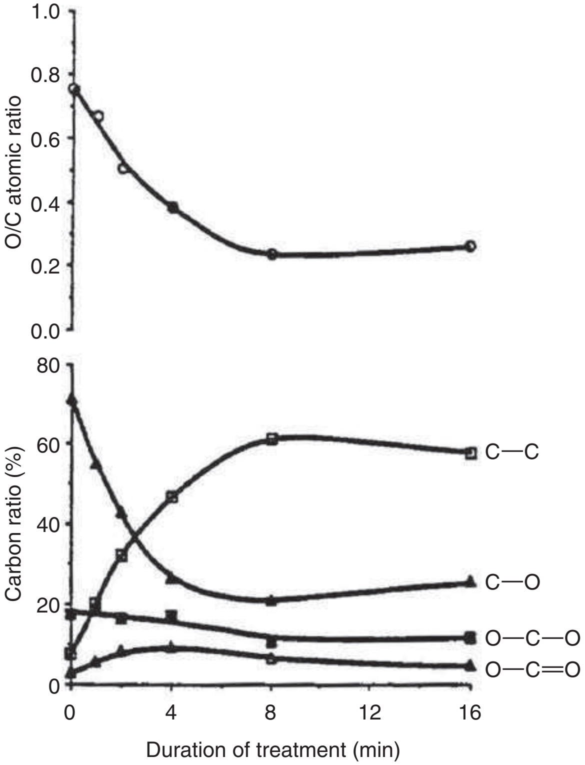
Wettability or intimate contact of a liquid adhesive to a solid substrate is necessary for durable bonding. The bond quality between a paint and a solid surface is also affected by the wettability. However, some wood species contain extractives that interfere with the adhesive bonding of the wood to other materials. They consist of hydrophobic resins, esters of fatty acids, waxes, etc. These substances form a structure of low surface energy at the wood surface. For this reason many papers concerning the pre-treatment of wood to improve its wettability and adhesive bonding have been reported.[90,91,93] Oxidative activation of resinous wood surfaces by a corona treatment to improve adhesive bonding was studied. It was found that the wettability of the veneers, including hardwoods, softwoods and tropical woods, increased with increasing treatment dose, and the gluability increased rapidly after the initial mild treatment. To elucidate the nature of any chemical change occurring on the wood surface, the dyeing of the wood and its components was performed and examined using Schiff's reagent. The results showed a higher dyeing ability for the corona-treated samples compared to the untreated ones, indicating that aldehyde groups were formed by the corona treatment. These were formed by oxidation of alcohol–benzene extractives on the wood surface. The untreated and corona-treated samples adsorbed basic dye to the same extent of coloration, indicating that no measurable carboxyl groups were formed by the treatment.[91] Atmospheric plasma, corona and fluorination were used to modify pine sapwood samples to improve the wet adhesion of water-borne acrylic dispersions.[89] All three methods improved the wet adhesion of the dispersions. This was attributed to the increased polar portion of the surface free energy. However, opposite to the observations made for the acrylate dispersions, the wet adhesion of the solvent-based internal comparison product (ICP) (according to EN 927-3) was reduced by the plasma treatment. The reason for this was not clarified, but it was stated that the plasma treatment has to be carefully fine-tuned to the coating material.[89]

10.6.2 Plasma surface modification of wood pulp fibres

Wood pulp fibres are traditionally characterised by bulk measurements, i.e. determination of chemical as well as physical characteristics of bulk fibres. However, since the surface of the fibres interact with each other and with other materials such as adhesives and barrier coatings and other liquids or gases, it is clear that controlling the surface composition and surface properties of such fibres and understanding their relation with the macroscopic physical properties is critical for further improvement of wood pulp fibres. Surface modification of the fibres is therefore an important tool for increasing this knowledge. Comparative evaluation of the effects of oxygen air, nitrogen and argon cold plasma treatments of chemithermomechanical pulp (CTMP) showed that, whereas oxygen and air plasmas increase substantially the wettability (in some cases more than 100%), nitrogen and argon discharges reduce wettability.[94,95] It was demonstrated that the oxygen plasma treatment increases the oxygen content of fibre surfaces. The wettability increase was related to the oxidation and removal of hydrophobic materials (e.g. fatty acids, resin acids) from fibre surfaces and to the simultaneous oxidation and scission of the lignin and carbohydrates from substrate surfaces. It was suggested that the highly oxidised low-molecular-weight materials might act as surfactants, decreasing the contact angle between the liquid and the pulp and thus enhancing the permeation rate into the fibre network. The effectiveness of oxygen plasma treatments on various cellulosic fibres (cotton, kraft pulp) under different discharge conditions was also evaluated.[96,97] It was shown that microwave plasma conditions can induce very significant improvements in wetting properties of kraft paper strips and that water-migration velocity depends greatly on the length of treatment time and on the nature of plasma gases. Oxygen plasmas produced the most significant effects, in treatment times as low as 5 seconds. However, argon and nitrogen discharges also lead to wettability improvements. It was suggested that oxidation is not the only reaction responsible for the process involving wettability changes. As shown in Figure 10.9, hydrogen plasma treatments cause the opposite effects on pure cellulosic and greaseproof paper substrates in comparison to oxygen-RF discharges.[98] It was demonstrated that hydrogen plasma reduces the oxygen-to-carbon



10.9 Adhesive strength of greaseproof paper–polyethylene laminates. Greaseproof paper exposed to hydrogen plasma (•) and to oxygen plasma (○). (Reproduced with permission from Ref. 61.)

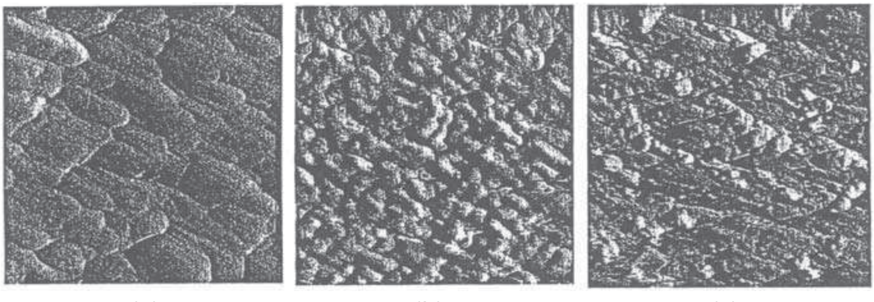


10.10 Hydrogen plasma treatment of filter paper. Changes in O/C atomic ratio and in the amount of the different carbons as a function of treatment time. (Reproduced with permission from Ref. 98.)

ratio and the number of hydroxyl groups on the cellulose, and generates low-molecular-weight compounds, see Figure 10.10. The water wettability of hydrogen plasma-modified pure cellulose is reduced as a result of lower surface polarity. However, the effect is opposite on paper substrates containing high amounts of resin. The oxygen plasma treatment of pure cellulose both oxidises and reduces the surface (macromolecular scissoring mechanisms associated with the formation of unsaturated and cross-linked structures), whereas hydrophobic-nature resin-rich paper substrates show improved water wettability after both oxygen and hydrogen plasma treatments.

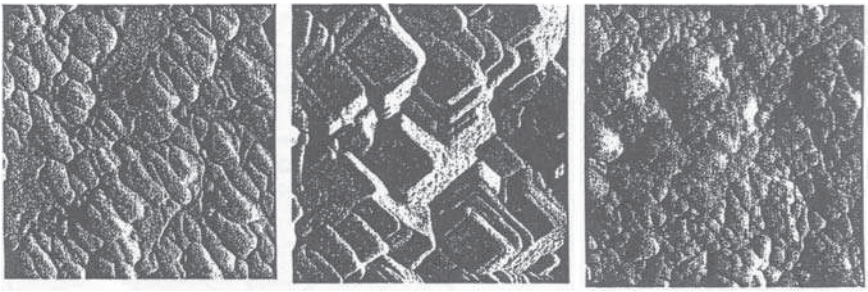
10.7 Plasma modification of man-made cellulosics

The energetic particles of cold plasmas interact intensely with the surface topographies of polymeric substrates in addition to free-radical generation and surface functionalisation mechanisms. It is well known that more- or less-ordered supramolecular structures (crystalline and amorphous zones) coexist in the polymeric substrates, and that the plasma-mediated etching reactions are morphology selective. This behaviour opens up possibilities for creating enhanced surface crystallinity and, consequently, new ways for initiation of template graft polymerisation reactions from plasma-activated surfaces. It has been demonstrated that argon-RF-plasma conditions can generate enhanced crystallinity and active sites (e.g. free radicals) simultaneously on cellophane film surfaces.[99] The free radicals can readily initiate template growth of polyacrylonitrile (AN) and styrene (ST) under *in situ* conditions, allowing for the creation of very thin and controlled-uniformity, ordered polymeric layers with potential applications in the optical industry. Detailed information on the ordered surface morphologies of the oxygen plasma-treated and AN- and ST-grafted cellophane was obtained by AFM investigations. Figures 10.11 and 10.12 show the AFM images of acetone-washed commercial cellophane, the oxygen plasma-exposed washed cellophane film and the oxygen plasma-treated and subsequently AN- and ST-grafted cellophane. It was concluded that acetone extraction of commercial cellophane clearly exposes the ordered nature of the cellulosic fibrils, and that the orientation of the grafted polymer crystallites strictly follows the orientation of the fibrils.[99] AFM was also used to evaluate the adhesion properties of untreated and plasma-modified cellophane films.[100] Both standard silicon nitride tips, as well as self-assembled monolayer (SAM) modified gold-coated tips containing a variety of specific functional groups, including —COOH and —CH_3 terminated tips, were used. Plasma treatments were used to modify the surface chemistry and surface roughness. However, neither oxygen nor argon plasma treatment caused significant changes in surface adhesion. It was apparent that the increased surface roughness caused by the plasma treatments cancelled out the enhancement



(a) (b) (c)

10.11 Atomic Force Microscopy images of cellophane (a) untreated, (b) argon plasma-treated for 30 seconds, and (c) argon plasma-treated for 9 minutes. (Reproduced with permission from Ref. 99.)



10.12 Atomic Force Microscopy images of cellophane grafted with polyacrylonitrile initiated from (a) argon plasma-treated cellophane surfaces for 30 seconds (b) argon plasma-treated cellophane surfaces for 9 minutes, and (c) cerium ion activation (conventional grafting) cellophane surfaces. (Reproduced with permission from Ref. 99.)

of the plasma-induced changes in surface chemistry. On the other hand, it was found that hydrazine plasma treatment of cellophane, introducing —NH_2 groups on the surface, resulted in strong adhesion forces to the —COOH-modified AFM tip due to acid–base interactions.[100]

Sheets of cellophane were corona-treated and the strength of water-induced bonds between the sheets was related to changes in solid surface free energy accompanying the treatment.[101] A significant increase in the surface free energy was primarily due to an increase in the polarity of the surface and a corresponding slight decrease in the magnitude of dispersion-type forces. Oxidation was found to be the primary chemical effect of the corona treatment and the modifications were confined within very thin surface layers.[101]

As already mentioned, cellophane has a low permeability to air, grease and bacteria, which makes it useful for food packaging. Cellophane films are often laminated with thermoplastics, such as polyethylene films, to further improve its protective properties, e.g. water and moisture barrier properties. However, the hydrophobic plastic matrix is inherently incompatible with the hydrophilic natural polymer. Therefore, surface treatments, including plasma and corona treatments, have been performed and evaluated by numerous authors.[1,102–104]

Viscose is a regenerated cellulosic fibre widely used in apparel, home furnishing and industrial materials.[12] Its characteristics include relatively low resiliency (particularly when wet), high moisture absorption, and soft hand. Viscose can be in either filament or staple form, and warp yarns must be sized before weaving to increase weavability. In general, a larger amount of size is used for viscose or viscose blends than for cotton yarns, and the size must be removed by wet processing prior to dyeing and finishing of the woven fabrics. From the chemical processing point of view, viscose requires a more careful treatment than, e.g. cotton, as it is more susceptible to chemical attack.[105] Since plasma treatments do not involve as large quantities of chemicals and water as conventional desizing, it is preferable to use this technique to desize viscose. Air–oxygen–helium and air–helium atmospheric-pressure plasma treatments were employed to desize polyvinyl alcohol (PVA) on a viscose fabric.[10] Both plasma treatments were able to remove some of the PVA on the viscose fabric and increase PVA solubility in cold water, resulting in higher weight loss in cold washing. The efficiency of the treatments increased with increasing treatment time. Plasma treatment followed by one cold and one hot wash had the same effect as conventional chemical treatments followed by two cycles of cold and hot washing. In addition, the atmospheric plasma did not have any negative effect on viscose tensile strength.[10]

Information on the adhesion characteristics (interfacial shear strength) of RF-oxygen plasma-treated viscose fibres and polyethylene have been obtained by using single-fibre fragmentation estimations evidenced by shear strength values and birefringence patterns.[62] It was found that the oxygen plasma treatments enhanced the interfacial shear strength and critical fibre length considerably. Fibre fragmentation occurs in a matrix until the critical fibre length is reached by fragmentation (i.e. when the fibre is too short to bear the load). It was demonstrated that the plasma-generated relative surface atomic composition (surface chemistry), surface energetics (dynamic contact angles) and surface topographies (SEM analyses) do not improve the adhesion. Instead, the enhanced adhesion was related to the covalent bond formation between the fibre and the matrix, a mechanism which was suggested to be mediated by hydroperoxide groups generated under oxygen plasma condition.[62] However, this theory has been questioned since the development of cross-linking reactions and the formation of covalent bonds between interfaces are difficult to relate only to the presence of hydroperoxide functionalities evaluated by SO_2 tagging. This is due to the fact that trapped free-radical sites also react spontaneously with sulphur dioxide.[1]

10.8 References

1. Denes F and Young R A, ‘Surface modification of polysaccharides under cold plasma conditions’, in Dumitriu S (Ed.), *Structural Diversity and Functional Versatility of Polysacchararides*, New York, Basel, Hong Kong, Marcel Dekker Inc., 1998.
2. Denes F, Young R A, Sarmadi M, ‘Surface Functionalization of polymers under cold plasma conditions’ – A mechanistic approach, *J. Photopolym. Sci. Technol.*, 1997 **10**(1) 91–112.

3. Wakelyn P J, *et al.*, 'Cotton fibers', in Lewin M and Pearce E M (Eds.), *Handbook of Fiber Chemistry*, New York, Basel, Marcel Dekker, 1998.
4. Bell T M and Gillham F E M, '*The World of Cotton*', ContiCotton, EMR, Washington, DC 1989.
5. Batra S K, 'Other long vegetable fibers', in Lewin M and Pearce E M (Eds.), *Handbook of Fiber Chemistry*, New York, Basel, Marcel Dekker, 1998.
6. Rowell R M and Stout H P, 'Jute and Kenaf', in Lewin M and Pearce E M (Eds.), *Handbook of Fiber Chemistry*, New York, Basel, Marcel Dekker, 1998.
7. Turner A J, in Urquhart A R and Howitt F O (Eds.), *The Structure of Textile Fibers*, The Textile Institute, Manchester, UK, 1953 91–117.
8. Carlsson C M G, PhD Thesis, *Surface composition of wood pulp fibres: relevance to wettability, sorption and adhesion*, Royal Institute of Technology, Stockholm, 1996.
9. Cellophane, www.wikepedia.com.
10. Cai Z, Uiu Y, Hwang Y J, Zhang C, McCord M, 'The use of atmospheric pressure plasma treatment in desizing PVA on viscose fabrics', *J. Industrial Textiles*, 2003 **32**(3) 223–232.
11. Dyer J and Daul G C, 'Rayon Fibers', in Lewin M and Pearce E M (Eds.), *Handbook of Fiber Chemistry*, New York, Basel, Marcel Dekker, 1998.
12. Kumar A and Purtell C, *Text. Chem. Colorist*, 1994 **26**(10) 25–28.
13. Varghese J, Pasad D M, Patel P B, *Colourage*, 1977 **24**(13) 23–28.
14. Tasker S, Badyal J P S, Backson S C E, Richards R W, 'Hydroxyl accessibility in celluloses', *Polymer*, 1994 **35**(22) 4717–4721.
15. Wakida T, Takeda K, Tanaka I, Takagishi T, 'Free radicals in cellulose fibres treated with low temperature plasma', *Textile Res. J.*, 1989 **Jan** 49–53.
16. Sabharwal H S, Denes F, Nielsen L, Young R A, 'Free-radical formation in jute from argon plasma treatment', *J. Agric. Food Chem.*, 1993 **41** 2202–2207.
17. Kuzuya M, Noda N, Kondo S-I, Noguchi A, *J. Am. Chem. Soc.*, 1992 **114** 6505.
18. Kuzuya M, Morisaki K, Niwa J, Yamauchi Y, Xu K, 'Spectrochemistry of polycarbohydrate free radicals generated by argon plasmolysis: effect of tertiary structure on free radical formation', *J. Phys. Chem.*, 1994 **98** 11301–11307.
19. Kuzuya M and Yamauchi Y, 'Plasma-induced free radicals of polycrystalline dicarbohydrates studied by electron spin resonance', *Thin Solid Films*, 1998 **316** 158–164.
20. Denes F and Young R A, 'Improvement in surface properties of lignocellulosics using cold-plasma treatment', in Prasad P N *et al.* (Ed.), *Science and Technology of Polymers and Advanced Materials*, New York, Plenum Press, 1998.
21. Hua Z Q, Sitaru R, Denes F, Young R A, 'Mechanisms of oxygen- and argon-RF-plasma-induced surface chemistry of cellulose', *Plasmas and Polymers*, 1997 **2**(3) 199–224.
22. McCord M G, Hwang Y J, Qiu Y, Hughes L K, Bourham M A, 'Surface analysis of cotton fabrics fluorinated in radio-frequency plasma', *J. Appl. Polym. Sci.*, 2003 **88** 2038–2047.
23. Vitta S B, Stahel E P, Stannett V T, *J. Macromol. Sci-Chem*, 1985 **A22** 579.
24. Abidi N and Hequet E, 'Cotton fabric graft copolymerisation using microwave plasma. II. Physical properties', *J. Appl. Polym. Sci.*, 2005 **98** 896–902.

25. Vohrer U, Müller M, Oehr C, 'Glow-discharge treatment for the modification of textiles', *Surface and Coatings Technol.*, 1998 **98** 1128–1131.
26. Jahagirdar C J and Tiwari L B, 'Study of plasma polymerisation of dichloromethane on cotton and polyester fabrics', *J. Appl. Polym. Sci.*, 2004 **94** 2014–2021.
27. Özdogan E, Saber R, Ayhan H, Seventekin N, 'A new approach for dyeability of cotton fabrics by different plasma polymerisation methods', *Color. Technol.*, 2002 **118** 100–103.
28. Jung H Z, Ward T L, Benerito R R, 'The effect of argon cold plasma on water absorption of cotton', *Textile Res. J.*, 1977 **Mar** 217–223.
29. Benerito R R, Ward T, Soignet D M, Hinojosa O, 'Modifications of cotton cellulose surfaces by use of radiofrequency cold plasmas and characterisation of surface changes by ESCA', *Textile Res. J.*, 1981 **Apr** 224–232.
30. Kubota S and Emori K, 'Modification of cotton fibre by low temperature plasma', *J. Photopolym. Sci. Technol.*, 1993 **6**(3) 353–360.
31. Kubota S and Emori K, 'Abrasive finishing of cotton fibre by low temperature plasma', *Sen-I Gakkaishi*, 1984 **50**(8) 343–348.
32. Bhat N V and Benjamin Y N, 'Surface resistivity behaviour of plasma treated and plasma grafted cotton and polyester fabrics', *Textile Res. J.*, 1999 **69**(1) 38–42.
33. Malek R M A and Holme I, 'The effect of plasma treatment on some properties of cotton', *Iranian Polymer Journal*, 2003 **12**(4) 271–280.
34. Raje C R, Gurjar R M, Kawlekar S R, 'Low temperature plasma treatment of cotton fabrics', *Colourage*, 2004 **May** 39–42.
35. Rashidi A, Moussavipourgharbi H, Mirjalili M, 'Effect of low-temperature plasma treatment on surface modification of cotton and polyester fabrics', *Indian Journal of Fibre & Textile Research*, 2004 **29** 74–78.
36. Sun D and Stylios G K, 'Effect of low temperature plasma treatment on the scouring and dyeing of natural fibres', *Textile Res. J.*, 2004 **74**(9) 751–756.
37. Zubaidi and Hirotsu T, 'Graft polymerisation of hydrophilic monomers onto textile fibres treated by glow discharge plasma', *J. Appl. Polym. Sci.*, 1996 **61** 1579–1584.
38. Selli E, Mazzone G, Oliva C, Martini F, Riccardi C, Barni R, Marcandalli B, Massafra M R, 'Characterisation of poly(ethylene terphthalate) and cotton fibres after cold SF_6 plasma treatment', *J. Mater. Chem.*, 2001 **11** 1985–1991.
39. Ward T L, Jung H Z, Hinojosa O, Benerito R R, 'Effect of RF cold plasmas on polysaccharides', *Surface Science*, 1978 **76** 257–273.
40. Chen J-R, 'Study on free radicals of cotton and wool fibres treated with low-temperature plasma', *J. Appl. Polym. Sci.*, 1996 **62** 1325–1329.
41. Abbott G M, 'The corona treatment of cotton', *Textile Res. J.*, 1977 **Feb** 141–144.
42. Stone R B and Barrett J R, 'U.S.D.A. study reveals interesting effects of gas plasma radiations on cotton yarn', *Textile Bull.* 1962 **88**(1) 65–69.
43. Thorsen W J, 'Temporary and permanent fibre-friction increases induced by corona treatment', *Textile Res. J.*, 1971 **41** 331–336.
44. Thorsen W J, 'Improvement of cotton spinnability, strength and abrasion resistance by corona treatment', *Textile Res. J.*, 1971 **41** 455–458.

45. Thorsen W J, ‘Modification of the cuticle and primary wall of cotton by corona treatment’, *Textile Res. J.*, 1974 **44** 422–428.
46. Sekar N, ‘Plasma treatment processes in textiles – an update’, *Colourage*, 2000 **Jun** 39–40.
47. Cai Z, Hwang Y-J, Park Y, Zhang C, McCord M, Qiu Y, ‘Preliminary investigation of atmospheric pressure plasma-aided desizing for cotton fabrics’, *AATCC Review*, 2002 **Dec** 18–21.
48. Cai Z, Qiu Y, Zhang C, Hwang Y-J, McCord M, ‘Effect of atmospheric plasma treatment on desizing of PVA on cotton’, *Textile Res. J.*, 2003 **73**(8) 670–674.
49. Sharnina L V, ‘Low-temperature plasma as the basis for creation of modern textile chemical technologies’, *Fibre Chemistry*, 2004 **36**(6) 431–436.
50. Temmerman E and Leys C, ‘Surface modification of cotton yarn with a DC glow discharge in ambient air’, *Surface and Coatings Technol.*, 2005 **200** 686–689.
51. Andreozzi L, Castelvetro V, Ciardelli G, Corsi L, Faetti M, Fatarella E, Zulli F, ‘Free radical generation upon plasma treatment of cotton fibres and their initiation efficiency in surface-graft polymerisation’ *J. Colloid Interface Sci.*, 2005 **289** 455–465.
52. Abidi N and Hequet E J, *J. Appl. Polym. Sci.*, 2004 **93** 145.
53. Sigurdsson S and Shishoo R, ‘Surface properties of polymers treated with tetrafluoromethane plasma’, *J. Appl. Polym. Sci.*, 1997 **66** 1591–1601.
54. D’Agostino R, Cramarossa F, Fracassi F, Illuzzi F, ‘Plasma polymerization of fluorocarbons’, in D’Agostino R (Ed.), *Plasma Deposition, Treatment, and Etching of Polymers*, San Diego, Academic Press, Inc., 1990.
55. Iriyama Y, Yasuda H, Yasuda T, Cho D L, ‘Plasma surface treatment of nylon fabrics by fluorocarbon compounds’, *J. Appl. Polym. Sci.*, 1990 **39** 249–264.
56. Markgraf D A, ‘Corona treatment: An overview 1986, *1986 Coextrusion Seminar Notes*, TAPPI Press, Atlanta, 85.
57. Liston E M, Martinu L, Wertheimer M R, *J. Adhes. Sci. Technol.*, 1993 **7** 1091.
58. Massines F and Gouda G, *J. Phys., D, Appl. Phys.*, 1998 **31** 3411.
59. Kutepov A M, and Zakharov A G, *Ros. Khim. Zh.*, 2002 **46** 103–115.
60. Zakharov A G and Maksimov, *Tekst. Khim.*, 1998 **1**(13) 42–46.
61. Carlsson C M G, and Strom G, ‘Adhesion between plasma-treated cellulosic materials and polyethylene’, *Surf. Interf. Anal.*, 1991 **17** 511–515.
62. Felix J M, Carlsson C M G, Gatenholm P, ‘Adhesion characteristics of oxygen plasma-treated rayon fibers’, *J. Adhes. Sci. Technol.*, 1994 **8** 163.
63. Felix J M, Gatenholm P, Schreiber H P, ‘Plasma modification of cellulose fibers: Effects on some polymer composite properties’, *J. Appl. Polym. Sci.*, 1994 **51** 285.
64. Carlsson C M G and Johansson K S, ‘Surface modification of plastics by plasma treatment and plasma polymerisation and its effect on adhesion’, *Surface and Interface Analysis*, 1993 **20** 441–448.
65. Bledzki A K, Reihmane S, Gassan J, ‘Properties and modification methods for vegetable fibres for natural fiber composites’, *J. Appl. Polym. Sci.*, 1996 **59** 1329–1336.
66. Couto E, Tan I H, Demarquette N, Caraschi J C, Leao A, ‘Oxygen plasma treatment of sisal fibres and polypropylene: Effects on mechanical properties of composites’, *Polym. Eng. Sci*, 2002 **42**(4) 790–797.

67. Martin A R, Denes F S, Rowell R M, Mattoso L H C, 'Mechanical behaviour of cold plasma-treated sisal and high-density polyethylene composites', *Polymer Composites*, 2003 **24**(3) 464–474.
68. Martin A R, Manolache S, Denes F S, Mattoso L H C, 'Functionalization of sisal fibres and high-density polyethylene by cold plasma treatment', *J. Appl. Polym. Sci.*, 2002 **85** 2145–2154.
69. Yuan X, Jayaraman K, Bhattacharyya D, 'Plasma treatment of sisal fibres and its effects on tensile strength and interfacial bonding', *J. Adhesion Sci. Technol.*, 2002 **16**(6) 703–727.
70. Yuan X, Jayaraman K, Bhattacharyya D, 'Mechanical properties of plasma-treated sisal fibre-reinforced polypropylene composites', *J. Adhesion Sci. Technol.*, 2004 **18**(9) 1027–1045.
71. Belgacem M N, Bataille P, Sapieha S, 'Effect of corona modification on the mechanical properties of polypropylene/cellulose composites', *J. Appl. Polym. Sci*, 1994 **53** 379–385.
72. Tu X, Young R A, Denes F, 'Improvement of bonding between cellulose and polypropylene by plasma treatment', *Cellulose*, 1994 **1** 87–106.
73. Bhattacharyya D, Yuan X, Jayaraman K, 'Plasma modification of natural fibres in polypropylene composites', *Int. J. Plastics Technol.*, 2003 **6** 27–31.
74. Yuan X, Jayaraman K, Bhattacharyya D, 'Effects of plasma treatment in enhancing the performance of woodfibre–polypropylene composites', *Composites – Part A: Applied Science and Manufacturing*, 2004 **35** 1363–1374.
75. Mahlberg R, Niemi H E-M, Denes F S, Rowell R M, 'Application of AFM on the adhesion studies of oxygen-plasma-treated polypropylene and lignocellulosics', *Langmuir*, 1999 **15** 2985–2992.
76. Strobel M, Jones V, Lyons C S, Ulsh M, Kushner M J, Dorei R, Branch M C, 'A comparison of corona-treated and flame-treated polypropylene films', *Plasmas and Polymers*, 2003 **8**(1) 61–95.
77. Flink P, and Stenberg B, *Br. Polym. J.*, 1990 **22** 147.
78. Ahlblad G, Kron A, Stenberg B, 'Effects of plasma treatment on mechanical properties of rubber/cellulose fibre composites', *Polym. Int.*, 1994 **33** 103.
79. Vladkova T G, Dineff P D, Gospodinova D N, 'Wood flour: a new filler for the rubber processing industry. II. Cure characteristics and mechanical properties of NBR compounds filled with corona-treated wood flour', *J. Appl. Polym. Sci.*, 2004 **91** 883–889.
80. Pettersen R C, in *The Chemistry of Solid Wood*, Washington DC, ACS 1984 57.
81. Rowell R M, in *The Chemistry of Solid Wood*, Washington DC, ACS 1984 175.
82. Feist W C and Hon D N-S, in *The Chemistry of Solid Wood*, Washington DC, ACS 1984 401.
83. Turkulin H, Richter K, Sell J, 'Adhesion of waterborne acrylic and hybrid paint on wood treated with primers', *Second Wood Coatings Congress*, The Hague, The Netherlands, 2000.
84. Cho D L and Sjöblom E, 'Plasma treatment of wood', *J. Appl. Polym. Sci.: Appl. Polym Symp.*, 1990 **46** 461–472.

85. Rehn P and Viöl W, 'Dielectric barrier discharge treatments at atmospheric pressure for wood surface modification', *Holz als Roh- und Werkstoff*, 2003 **61** 145–150.
86. Magalhaes W L E and de Souza M F, 'Solid softwood coated with plasma polymer for water repellence', *Surface and Coatings Technol.*, 2002 **155** 11–15.
87. Denes F, Sitaru R, Young R A, 'Template polymerization from cold-plasma-enhanced-crystallinity polymer surfaces', *J. Photopolym. Sci. Technol.*, 1998 **11**(2) 299–306.
88. Setoyama K, 'Surface modification of wood by plasma treatment and plasma polymerisation', *J. Photopolym. Sci technol.*, 1996 **9**(2) 243–250.
89. Lukowsky D, and Hora G, 'Pretreatments of wood to enhance the performance of outdoor coatings', *Macromol. Symp.*, 2002 **187** 77–85.
90. Rehn P, Wolkenhauser A, Bente M, Förster S, Viöl W, 'Wood surface modification in dielectric discharges at atmospheric pressure', *Surface and Coatings Technology*, 2003 **174–175** 515–518.
91. Sakata I, Morita M, Tsuruta N, Morita K, 'Activation of wood surface by corona treatment to improve adhesive bonding', *J. Appl. Polym. Sci.*, 1993 **49** 1251–1258.
92. Podgorski L, Chevet B, Onic L, Merlin A, 'Modification of wood wettability by plasma and corona treatments', *Int. J. Adhesion Adhesives*, 2000 **20** 103–111.
93. Chen H Y and Zavarin E, 'Interactions of cold radio frequency plasma with solid wood. I. Nitrogen permeability along the grain', *J. Wood Chem. Technol.*, 1990 **10**(3) 387–400.
94. Carlsson C M G, Strom G, Eriksson I, Lindström E, 'Improved wettability of chemithermomechanical pulp by oxygen plasma treatment' *Nordic Pulp & Paper Res. J.*, 1994 **9** 72–75.
95. Carlsson C M G, Strom G, Annergren G, 'Water sorption and surface composition of untreated or oxygen plasma-treated chemical pulps', *Nordic Pulp & Paper Res. J.*, 1995 **1** 17–23 + 32.
96. Benerito R R, Ward T L, Soignet D M, Hinjosa O, *Text. Res. J.*, 1981 **51** 224.
97. Chan Tang T W and Bossio R G, *Tappi*, 1980 **63** 111.
98. Carlsson C M G, and Strom G, 'Reduction and oxidation of cellulose surfaces by means of cold plasma', *Langmuir*, 1991 **7** 2492–2497.
99. Denes F, *et al.*, *Proceedings of the First International Symposium on Lignocellulosics–Plastics Composites*, Mar 13–15, Sao Paulo, Brazil, 1996.
100. Zhang X, and Young R A, 'Adhesion properties of cellulose films', *Mat. Res. Soc. Symp.*, Materials Research Society, 2000.
101. Brown P F and Swanson J W, 'Wetting properties of cellulose treated in a corona discharge', *Tappi*, 1971 **54**(12) 2012–2018.
102. Nielsen L D, Denes F, Young R A, 'Epitaxial growth of polyacrylonitrile on cellulose by plasma-induced polymerisation', *Polymeric Materials Science and Engineering*, 1996 **74** 408–409.
103. Nielsen L D, PhD Thesis: *A comparative study of plasma-induced polymerisation and plasma-state polymerisation of acrylonitrile for modification of cellophane* University of Wisconsin-Madison, Department of Forestry, 1995.

104. Bhat N V, and Makwana D N, 'Effects of plasma treatment on electrical conduction, weight loss and dye uptake in cellophane film', *J. Polym. Mater.*, 1991 **8** 153–156.
105. Varghese J, Pasad D M, Patel P B, *Colourage*, 1977 **24**(13) 23–28.

11

Plasma treatments of fibres and textiles

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11.1 Introduction

Cold plasma technologies have found extensive application in material processing for over 30 years and they are now widely used in the manufacture of semiconductors, magnetic media and special glasses, and for metal coating, etc. The success of these techniques is related to their ability to change the surface properties of a material by physical or chemical modification of its most external layers (≤1 μm), without modifying its bulk characteristics. In this way, reengineering of surface chemistry can open completely new fields of application to conventional polymers.

If we consider that, in many cases, the use of textiles is mainly determined by their surface properties, as a consequence of their very large specific areas, and that the traditional finishing methods usually involve high energy consumption, large amounts of chemical substances, frequently toxic or noxious, or use of organic solvents, as well as production of liquid and gaseous effluents which require expensive purification treatments, cold plasma processes seem to be very suitable for application in the textile industry. In fact, they are 'dry' processes; the amounts of chemicals required is very limited; in many cases the expected results are obtained just by using air, nitrogen, oxygen or other 'inert' gases. Moreover, they are rapid, extremely versatile and work at room temperature, thus limiting the amount of energy necessary for heating water or for inducing chemical reactions, typical for conventional processes, and can be applied to all kind of textiles, even to such delicate natural fibres as silk. All these points have induced, since the 1970s, a strong interest by various research groups, both academic and industrial. However, due to a multiplicity of factors, which will be discussed later in this chapter, plasma has not found the same success in the textile sector as it has in other industrial sectors.

On the other hand, the growing concern of final consumers and public authorities for environment and health aspects, the increasing requests for high-performance textiles, the extension of the use of textile materials to new sectors (building, geotextiles, medical uses, etc.) with special exigencies, has stimulated, during the last decade, a renewed interest for these technologies. Nowadays, plasma treatments are used in specific textile market niches, but it is easy to forecast their adoption also for products intended for wider markets.

11.2 Principles of plasma processes

A commonly accepted definition of plasma is: a partially ionised gas composed of highly excited atomic, molecular, ionic and radical species, as well as photons and electrons. Plasmas are generally classified as thermal or non-thermal. Thermal ('hot') plasmas are characterised by a condition of thermal equilibrium between all the different species contained in the gas. In fact, if the gas density is sufficiently high, the frequency of collisions between electrons, ions, and neutral species composing the plasma is such that an efficient energy exchange is possible. In thermal plasmas, temperatures of several thousands degrees are reached. It is clear that these plasmas are, intrinsically, of a destructive nature and no material can stand their action.

Contrary to thermal plasmas, non-thermal plasmas are 'cold' plasmas and are produced at room temperature or a little above room temperature. In this case, electrons acquire higher energies than ions and molecules, their energies ranging from 0.1 to some electron volts, and, due to the low density of the gas, collisions with the other species are relatively rare and thermal equilibrium is not reached: the bulk temperature of the gas is comparable to room temperature. Electron collisions with neutral species produce additional electrons and ions. Thanks to the low operating temperatures, cold plasmas can be put in contact with any material, even delicate textiles, without problems.

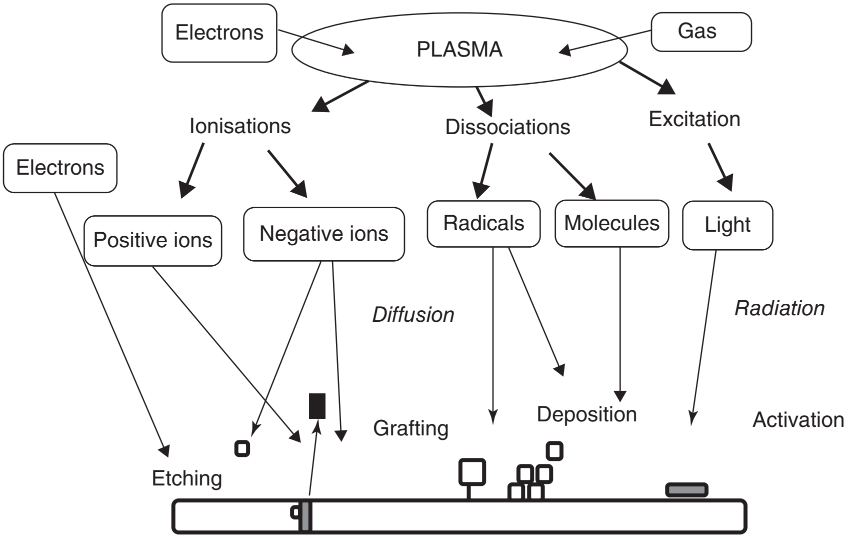
Different types of cold plasma can be described:

- *Glow discharge*: This is obtained at low pressures, typically less than 10 mbar. The plasma is generated by antennas, fed with electromagnetic fields at frequencies of 40 kHz or 13.56 MHz or microwaves (2.45 GHz).
- *Corona discharge*: This is obtained at atmospheric pressure by applying d.c., low frequency or pulsed high voltage between two electrodes of very different sizes. The corona consists of a series of rapid, non-uniform, non-arcing discharges. Plasma density drops off rapidly with increasing distance from the electrode.
- *Dielectric barrier discharge*: This is an atmospheric-pressure plasma source. In this case a pulsed high voltage is applied between electrodes, one or both of which is covered by a dielectric layer. The purpose of

the dielectric layer is to terminate rapidly the arcs that form in the region between electrodes. The discharge consists of series of rapid microdischarges.
- *Atmospheric pressure plasma jet (APPJ)*: This a non-thermal, atmospheric pressure, glow discharge plasma produced in continuously flowing gases (Park, 2000).

The interaction between the very active chemical species (and photons) present in the plasma gas and a substrate is the basis of all industrial applications of the above technologies. As a consequence of the very complex and non-equilibrium nature of cold plasmas, a multiplicity of very different phenomena can occur, depending on the nature of the gas and the operating conditions (Figure 11.1). Being interested in textile plasma processing, our attention will be limited to polymeric materials.

- **Cleaning** or **etching**: For such a phenomenon to occur, 'inert' gases (Ar, He, etc.), nitrogen or oxygen plasmas are typically used. The bombardment of the substrate with the plasma species causes the breakdown of covalent bonds. As a consequence, detachment of low molecular weight species (ablation) takes place. In this way, contaminants or even thin layers of the substrate are removed, producing extremely 'clean' surfaces, modifications in the surface area, or controlled reduction of weight of the exposed substrate.
- **Activation**: Interaction with plasma may induce the formation of active sites on the polymer surface (radicals or other active groups, such as



11.1 Cold plasma process.

hydroxyl, carboxyl, carbonyl, amine groups), which can give rise to chemical reactions, not typical of the untreated material, with substances brought in contact with the material after plasma processing.

- **Grafting**: Radical species present in the plasma may be directly grafted onto the polymer surface.
- **Polymerisation**: by using specific molecules, a process known as plasma-enhanced chemical vapour deposition (PECVD) may occur. These molecules, activated in the plasma, may react with themselves forming a polymer directly on the surface of the substrate. Depending on the different experimental conditions, chemically unique, nanometric polymeric coatings are obtained and chemical, permeation, adhesion and other properties of the starting material can be dramatically modified.

All these phenomena are limited to the most external layer of the substrate. Normally, the effects do not involve layers deeper than 10–100 nm. However, it must be noticed also that ultraviolet (UV) or vacuum ultraviolet (VUV) radiation (with wavelength <200 nm) is an important component of plasma. VUV radiation can give rise to a variety of photochemical interactions with the substrate, such as bond breakage and formation of free radicals, reaching inner layers (>10 nm) depending on the absorption coefficient of the substrate (Molina, 2003).

11.3 Plasma textile treatments

Plasma treatments of textiles, especially in the last ten years, have been extensively studied. A very large number of papers has been published and patents registered on this subject, all focussing on different aspects of plasma processing, such as:

- Generators and experimental set-ups
- Gas composition
- Types of textiles
- Plasma treatments for textile finishing
- Product innovation.

It is practically impossible to review such an amount of information in a thorough way. Therefore, only a general classification will be attempted, starting from the nature of the modifications that may be produced on textile materials. It should be kept in mind that, thanks to the high reactivity of the plasma environment, special results can be obtained on all textile materials:

- *Enhancement of both hydrophilic and hydrophobic properties.* This is one of the most widely studied plasma applications. Oxygen, ammonia, air, nitrogen, etc. plasmas have been used to increase the wettability of synthetic polymers (PA, PE, PP, PET, PTFE, etc.), while hydrophobic or oleophobic finishing of natural fibres (cotton, wool, silk, etc.) has been obtained by using siloxanes, perfluorocarbons, SF_6, acrylates, etc.

- *Adhesion promotion.* Good adhesion between fibres and matrix is essential in the production of composites and laminates. Plasma treatments can increase markedly the surface energy of synthetic fibres, improving the mechanical characteristics of the final products.
- *Dyeing and printing.* Several studies have shown that dyeability or printability of textiles can be markedly improved by plasma treatments. This effect can be obtained on both synthetic and natural fibres. Capillarity improvement, enhancement of surface area, reduction of external crystallinity, creation of reactive sites on the fibres and many other actions can contribute to the final effect depending on the operative conditions. Also production of colours on fibres exploiting diffraction effects has been attempted.
- *Electrical properties.* Antistatic properties have been conferred to artificial or synthetic polymers. Moreover, studies have been carried out for the creation of fabrics with very high conductive properties, suitable for integrating electronic devices into fabrics.
- *Intelligent filtration properties.* Filtration of gases or liquids is one of the most common technical applications of fibres, fabrics or non-wovens. Appropriate surface functionalisation can enhance chemical selectivity of traditional filters based on more conventional adsorption/absorption or physical separation processes.
- *Other properties.* The extreme versatility of the plasma processes is shown by a very large number of investigations concerned with a wide range of different properties of great importance for textiles, such as flame retardancy, crease resistance, antimicrobic, antimicotic, biological compatibility, antifelting for wool, UV-protection, as well as ‘hand’ modification, softening and antipilling.

Even if plasma treatments, in principle, may apply to all substrates, a clear description of the applications of plasma technologies to textiles requires a more specific examination from the point of view of the nature of the treated fibres. Due to the extreme variety of textiles, attention will be focussed on the most used materials and on synthetic fibres and silk in particular. As stated before, the number of papers dealing with plasma treatments of all types, and on practically all textile materials, is enormous and it is impossible to give an exhaustive report of all. Only a short survey will be attempted, trying to give a general picture of the state of the art of the research in this field. Table 11.1 reports a summary of some of the properties that plasma treatments can impart to material textiles.

Table 11.1 Some properties of textile materials that can be modified by plasma treatments

Property	Material	Treatment
Wettability	Synthetic fibres	Oxygen, air, NH_3
Hydrophobicity	Cellulosic fibres, wool, silk, PET	Fluorocarbons, SF_6, siloxanes
Dyeability	Synthetic fibres, wool, silk	Oxygen, air, nitrogen, argon, SF_6, acrylates
Flame retardance	Cellulosic fibres, synthetic fibres	Phosphorus compounds
Softness	Cellulosic fibres	Oxygen
Wrinkle resistance	Wool, silk, cellulosic fibres	Nitrogen, siloxanes
Antistaticity	Synthetic fibres	Chloromethylsilanes, acrylates
Adhesiveness	Synthetic fibres, cellulosic fibres	Air, oxygen, nitrogen, argon, acrylates
Antibacterial, antimicotic	Cellulosic fibres, synthetic fibres	
Bleaching	Wool	Oxygen
Antifelting	Wool	Oxygen, air

11.3.1 Synthetic fibres

In the field of synthetic fibres, plasma technologies have been mainly used for increasing hydrophilicity, conferring antistatic properties, improving dyeability and printability, as well as promoting adhesiveness for the preparation of composites and laminates.

Polypropylene (PP) is a widely used material, especially for technical applications. In many cases, an improvement of its hydrophilic properties would be quite useful; for instance, PP non-woven filters can be permeable to water only when high pressure is applied. The introduction of hydroxyl, carboxyl, carbonyl, amino groups by air, oxygen, nitrogen or NH_3 plasma can produce a very large increase in wettability. Both atmospheric and vacuum plasmas have been used (Sparavigna, 2002). The same effect is produced on all kinds of synthetic hydrophobic fibres such as polyethylene (PE), poly(ethylene terephthalate) (PET), polytetrafluoroethylene (PTFE), polyamides (PA), and so on. Usually the treated samples show also an improvement in antistatic and adhesive properties (Hautojarvi, 2000; Yip, 2002). Some experimental data of water contact angles are reported in Table 11.2 (Sparavigna, 2002).

The behaviour changes observed after oxygen plasma treatments are due to the formation of new polar groups on the surface, such as carbonyl

Table 11.2 Effect of air plasma treatment on water contact angle of some synthetic fibres

Material	Water contact angle	
	Untreated	Air plasma treated
PP	87°	22°
PE	87°	42°
PA	63°	17°
PET	71°	18°
PTFE	92°	53°

(Sparavigna, 2002)

(>C═O), carboxylic (—COOH), hydroxyl (—OH), and peroxide (—COO—R) groups. Nitrogen containing plasmas give rise to amino (—NH_2), imino (—CH═NH), cyano (—C≡N) groups. Moreover, plasma induces the activation of the surface, thus producing further carbon, oxygen and nitrogen functionalities as a consequence of the reactions of the activated layer when put in contact with atmospheric air. This effect is particularly evident on samples treated with inert gas plasmas (Denes, 1997).

The poor dyeability of PP and PE fibres, as well as many other fibres such as aramidic fibres, is one of the problems which impair a wider use of these fibres in non-technical textile sectors. It is well known that only the introduction of disperse dyes for coloration of PET opened an immense market to this fibre, so that now the production of synthetic fibres has overtaken that of natural fibres. Analogously, poly(acrylonitrile) (PAN) found good access to the market only when, instead of homopolymers, functionalised copolymers were used, so that dyeing with basic dyes could be carried out according to conventional methods.

As stated previously, plasma treatments are able to increase wettability of synthetic polymers in a dramatic way and are able to create specific reactive groups on the surface. These facts have been exploited to increase dyeability. In particular, PET, PA, PP have been the main object of interest. For PET, good results have been obtained with oxygen or air plasmas. An increase of colour depth with respect to untreated samples of up to 60% (Urbanczyk, 1983; Sarmadi, 1993; Yoon, 1996; Kan, 1998; Barni, 2005; Raffaele-Addamo, 2006) was observed. Interesting results have also been obtained, using argon plasma, for aramid fibres, where the increase in depth of shade seems to be due to a decrease in reflectivity of the surface as a consequence of the formation of micro/nanocraters (Kobayashi, 1995). Even if many research groups, working under widely different experimental conditions, have obtained remarkable dyeability increases, the reasons for such behaviour are still the object of some discussion. Modification in crystallinity of the external layer of the fibres (Okuno, 1992), increase in surface area brought about by ion bombardment, increase of polar interactions between polymer and dyes, creation of active sites, simple optical effects due to a lower reflectivity of the polymer, have all been proposed in order to explain the experimental results. Probably, attribution of the observed behaviour to one single cause is not realistic. On the other hand, an increase of hydrophobicity may also be of great interest for special applications. PET fibres have been shown to increase adhesion strength to a PE matrix from 1 to 2.5 N/mm using an ethylene plasma (Höcker, 2002). Siloxane, perfluorocarbon, SF_6 have given very interesting results. The low resistance to hydrolysis of polyaramid fibres can be markedly reduced by application of a hexafluoroethene/hydrogen plasma, which creates a hydrophobic diffusion barrier layer at the surface of the fibre.

Grafting of vinyl monomers has also been the object of many studies for a very wide range of applications. This method, in fact, opens the way to the introduction of special functionalities with extremely diversified reactivities. Yarn or fabric properties can thus be re-engineered according to a specific project for special uses (Oktem, 1999; Hochart, 2003; Liao, 2004; Möller, 2006). Incorporation of vinyl monomers can be achieved following two different approaches. In the first, the fabrics are directly treated in a monomer plasma, while in the second, preliminary argon, or other non-depositing gas, plasma treatment is performed in order to activate the surface by producing active sites, and, immediately after treatment, the fabric is put in contact with monomer vapours or immersed in a bath containing the monomer. The second of these procedures has been the most studied. According to this method, flame-retardant properties (Shi, 2000), reduction of resistivity, modifications in wettability, dyeability, adhesivity, etc. have been given to synthetic fibres (Bhat, 1999; Tyan, 2002, Tyan, 2003, Cai, 2003).

The demand not only for antistatic textiles, but also for electrically conductive textiles, is rapidly growing for a number of applications, such as electromagnetic shielding materials, building materials and smart textiles. Introduction on the substrate surface of basic functionalities has been found to be very effective for promoting metal–fabric adhesion (Šimor, 2003). Very short contact times (0.1 s) have been shown to be sufficient for optimum results (Charbonnier, 1996). Plasma treatments have been also been used to promote compatibility with organic conductors, such as polythiophene, polyaniline and polypyrrole (Oh, 2001).

Grafting of various silane monomers has imparted to synthetic fibres increased thermal stability, scratch or crease resistance and colour depth (Akovali, 1990; Ganapathy, 1966; Lee, 2001). Air plasmas have been found to be very effective for sterilisation of PP non-woven fabric structures

(Kang, 2004). Bacterial proliferation on synthetic fibres is the object of strong interest not only for biomedical applications, but also for avoiding formation of bad smell or fibre degradation (Kim, 2002). The bacterial inactivation efficiency of silver metal and oxides is very well known. Ag-loaded PET-PA fabrics with very good permanent antibacterial properties have been prepared by activation with RF air plasma treatment followed by chemical reduction of silver salts (Yuranova, 2003). Acrylic acid grafted on PP activated by oxygen low-pressure plasma has been used as a support to promote chitosan immobilisation on the fibre through formation of amine bonds. The modified PP non-woven fabric showed marked anticoagulation and cell-adhesion properties (Tyan, 2003).

11.3.2 Cellulosic fibres

Cotton is one of the most used substrates for studying the application of plasma treatments to textiles. Low temperature plasmas of air, argon and oxygen are able to increase strongly water absorption, soil release, drying rate, crease resistance properties, but do not improve markedly the dyeability of cotton (Goodman, 1960; Stone jr, 1962; Ward, 1979; D'Agostino, 1982; Benerito, 1981; Wakida, 1989; Chen, 1991; Chen, 1996).

Cotton fabrics treated with plasmas of fluorocarbon gases, such as tetrafluoromethane (CF_4), tetrafluoroethane/hydrogen or hexafluoropropene (C_3F_6), show a strong increase in water contact angles and wet-out times (McCord, 2003; Zhang, 2003). Very good results were also obtained with SF_6 plasma (Raffaele-Addamo, 2003). In this case, direct binding of fluorine atoms to cellulose polymer chains occurs. The resulting effects are quite stable. Treatment with hexamethyldisiloxane (HMDSO) leads to a very strong hydrophobisation effect with a water contact angle of greater than 130º (Höcker, 2002).

In order to enhance dyeability, good results can be obtained by introducing onto cotton cationic functionalities, so reducing the negative zeta-potential in water. Ammonia or other amine substances, such as ethylenediamine (EDA) or triethylenetetramine (TETA), have been used (Kamel, 1998; Blanchard, 1999; Ozdogan, 2002).

Surface activation and subsequent grafting of acrylic monomers on cellulosic fibres has been the object of many investigations (Zubaidi, 1996; Bhat, 1999; Andreozzi, 2005). Grafting of acrylamide was found to reduce significantly the surface resistivity of cotton, marginally increasing water absorption, while use of acrylonitrile monomers led to a slight increase of surface resistivity (Bhat, 1999). Use of vinyl laurate monomer gives rise to very high water repellence properties which induce strength losses much lower than those experienced with traditional resin finishing (Abidi, 2004; Abidi, 2005).

A further stage of cotton processing where plasma technologies can find useful applications is desizing. Atmospheric air, air/He and, especially, air/O_2/He plasma etching, followed by hot water washing, was found to be very effective for complete removal of polyvinyl alcohol (PVA), used as sizing agent, without affecting fabric properties. The positive action is due to breakdown of PVA molecular chains, thus facilitating swelling and dispersing in water (Cai, 2003).

11.3.3 Wool and silk

Wool was one of the first fibres for which industrial application of plasma technologies were attempted. In fact, the first patent describing a corona treatment on wool goes back to 1956. The main object of study is shrink-proofing of wool (Rakowski, 1996).

Air or oxygen plasma treatments, either at atmospheric and low pressure, have proven very effective in conferring antifelting properties to wool fabrics, even if, at the present state of research, the quality and durability of the fabrics treated by the chlorine/Hercosett method are still superior under various aspects. In particular, plasma-treated fabrics show a harsher hand, a decrease of tear strength and often an unpleasant odour that must be removed by subsequent washing. The latter effect is probably due to oxidation of wool fatty substances. Post-application of some silicone polymer softeners or resins can overcome these drawbacks and can further improve dimensional stability and wrinkle resistance (Kim, 2002) reaching quality levels not inferior to the chlorine/Hercosett system. Electron spin resonance (ESR) studies have shown that nitrogen, air and water vapour plasma treatments of wool produce two new signals, attributable to an organic (carbon or oxygen) radical and to a nitrogen radical (consistent with nitroxide radicals) whose central band is overlapped by the organic radical. No sulphur radical formation was detected (Molina, 2003).

Air and nitrogen plasmas produce significant effects on wool dyeing with acid dyes. Increased dyeing kinetics, improved bath exhaustion and enhanced depth of shade have been observed (Höcker, 1994). Formation of additional amino groups is likely to be at the origin of the phenomenon (Holme, 2000).

As far as silk is concerned, the number of studies regarding this fibre is much more limited. Nitrogen plasma induces formation of microcraters on the surface of the fibre if the treatment is carried out under relatively drastic conditions, while no effect is visible by scanning electron microscopy for short contact times (less than 1 min) or lower RF power (less than 50 W). However, even very short contact times induce large increases in colour depth (more than 30%) upon dyeing with acid dyes. This effect decreases with increasing exposure times. However, dye absorption in plasma-treated samples was always greater than in untreated ones under the experimental conditions adopted (Massafra, 1996). Tetramethyldisiloxane (TMDSO) and TMDSO/O_2 plasmas give rise to a layer of silicon polymer or silica deposited over the surface of the fibres which, under the experimental conditions adopted, makes fibroin insoluble in conventional silk solvents (saturated LiBr solution) and improve significantly wrinkle recovery and flame resistance properties. Acid dye absorption is slightly increased in TMDSO plasma treated samples while it is slightly reduced by using TMDSO/O_2 plasma (Massafra, 1996).

Water repellence is produced, both on wool and silk, by fluorinating plasmas, such as SF_6 or fluorocarbons (Selli, 2001b; Chaivan, 2005). Water contact angles comparable (>130°) to those of polystyrene, poly(tetrafluoroethylene), silicone, etc. can be obtained with short treatment times, but the results are strongly influenced by the experimental conditions. It is interesting to note that the most hydrophobic samples reveal also an increase in surface fibroin crystallinity and in microroughness. Probably fluorine implantation is accompanied by etching, especially of the surface amorphous polymeric regions. The samples that show such a combination of effects are also characterised by the greatest increase in water contact angles and a longer stability of the water repellence properties.

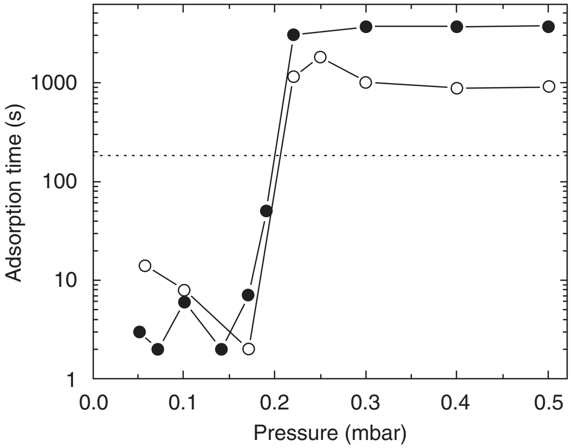
Air and oxygen plasmas have also been used as a pre-treatment in the silk degumming process. The time necessary to remove completely sericin was dramatically reduced, both in the case of the traditional Marseilles soap bath method and in the case of the high-pressure water bath technique.

11.3.4 Influence of operative conditions

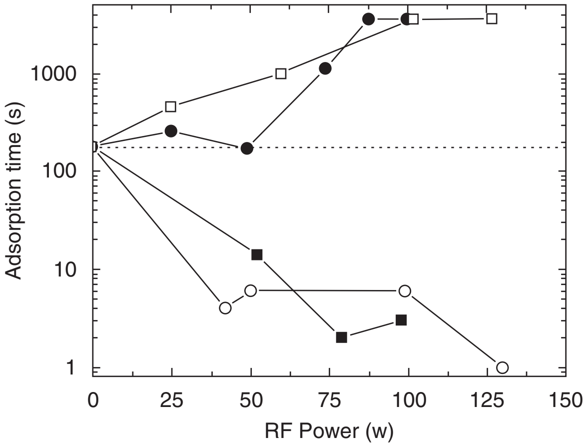
Even if the short survey reported above shows that plasma processing has all the characteristics for being successfully and profitably employed in textile manufacture, nevertheless textile industrial applications are still far from being common. Many factors are at the origin of this fact. When dealing with plasma treatments, it should be kept in mind that the effects obtained in practice, even on the same substrate, depend on a multiplicity of factors and not only on the gas used. The experimental set-up plays a major role. Variations in gas pressure, frequency and power of the generator, geometry of the electrodes and of the reaction chamber, treatment time, and so on, can affect the results in an extraordinary way. Plasma chemistry is extremely complex and cold plasmas are in a non-equilibrium state. Plasma is a state of matter, just like the liquid state, and cannot be considered as something exactly defined simply by its macroscopic composition. In order to obtain reproducible and predictable results, it is necessary to have a good knowledge of the nature of the reacting species present in the plasma, their concentrations and space distribution inside the reactor, as well as of the reactivity of the various species with the substrate. Some examples can be described to clarify this point.

As cited above, radio frequency (RF) low-pressure SF_6 plasma treatment is known to increase hydrophobicity of polymer surfaces (Riccardi, 2001; Selli, 2001a; Cruz-Barba, 2002; Raffaele-Addamo, 2003; Ranger, 2003; Barni, 2005). As shown in Figure 11.2, enhanced hydrophobic properties of PET could be observed only at pressures higher than 0.2 mbar. At lower pressures, on the contrary, a very sharp transition occurs and an unexpected increase in hydrophilicity takes place. If RF power or treatment times are changed, the above effects both increase, hydrophilicity under 0.2 mbar and hydrophobicity above that threshold limit (Figure 11.3). SF_6 plasma treatment can also produce modifications of dyeability of PET, as happens with other gases (air, argon, oxygen, etc.), but here again a strong increase of dyeability at low pressure and a decrease at higher pressures is observed (Figure 11.4). In the case of PET, dyeability has been related to hydrophilicity and/or increase or microroughness and surface area. The explanation of the observed phenomena is relatively simple only if a careful diagnostic of the plasma has been carried out and discharge local properties and prevailing reactions with polymer surface have been characterised.

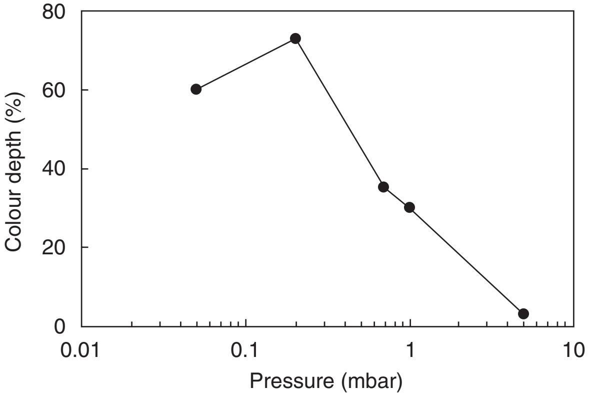
Hydrophobicity is produced by fluorination of the polymer. The reactive species are fluorine atoms. Under relatively low pressure, the ionisation degree is higher and the surface is mainly affected by collisions with electrons and ions. Thus, etching and activation processes are prevalent, leading to an increase in surface area and formation of hydrophilic functional groups. Under higher pressures, the mean free path of electrons and ions is lower; the number of collisions with the surface and impact energy are



11.2 Water droplet adsorption time values of SF_6 plasma-treated PET samples at different pressures (● 100 W ○ 50 W).



11.3 Water droplet adsorption time values of SF_6 plasma treated PET samples at different RF power (■ 0.05 mbar ○ 0.10 mbar ● 0.22 mbar □ 0.40 mbar).



11.4 Percentage increase of colour depth of PET fabrics dyed after air plasma treatments at different pressures.

reduced. Fluorine grafting is now prevailing and surface area is comparable with that of untreated samples.

Also, the distance of the substrate from the electrodes can influence strongly the result, as well as can the form and size of the reactor, as a consequence of the variations in spatial distribution of reactive species.

Moreover, textiles are very complex materials. The textile production chain is very long and, usually, the operators of any single stage are not fully aware of the treatments previously undergone by the material they are working on. Therefore, the substrates can introduce into the plasma chamber unexpected substances in unexpected quantities, which can modify substantially the final effects. Laboratory tests are usually carried out on carefully cleaned, washed and dried materials and do not take into account possible interferences brought about by the presence of contaminants. Even water can be considered, in some cases, as a contaminant and alter the results. Moreover, the structure, the weight and the texture of the treated material can markedly change the results when operating under the same experimental conditions.

Nowadays, in the textile field, atmospheric plasma treatments seem to attract more interest because they avoid complications and costs connected with vacuum production and greater possibilities of in-line continuous application. Corona discharge and, from the 1990s, dielectric barrier discharge and APPJ have been objects of great interest. However, all these processes, in different degree, produce less uniform effects and, usually, are not as rapid as vacuum processes. Furthermore, if the gas to be used is not simply air, the costs of reagents increase significantly. In any case, good knowledge of plasma chemistry and physics is still necessary in order to obtain the desired results.

11.4 Advantages and problems of plasma treatments for textiles

As has been demonstrated, plasma treatments of textiles look very promising. They can be used both in substitution of conventional processes and for the production of innovative textile materials with properties that cannot be achieved via wet processing. They are applicable, in principle, to all substrates, even to those that cannot be modified by conventional methods. In general, no significant alteration of bulk properties is produced. They are fast and extremely gentle, as well as environmentally friendly, being dry processes characterised by low consumption of chemicals and energy. When they cannot replace an existing wet process (dyeing and some finishing), if used as pre-treatments, they can reduce markedly the amount of chemicals required by the process and the concentration of pollutants in the effluents.

Nevertheless, the application of plasma treatments to textiles is still limited to technical products. Several explanations can be given. As specified above, correct application of plasma processes requires a good knowledge of the physical and chemical nature of plasmas, especially if the treatments have to be applied to different materials, as is the normal case for most textile small and medium enterprises. Therefore, skilled labour is required, which is, however, not generally available either in textile or in textile machinery companies. Without the capacity to understand the nature of the problems that can occur and to adopt the relevant correct actions, plasma treatments may lack reproducibility and give rise to disappointment and delusion. Moreover, the very wide variety of plasma technologies makes it difficult to decide which is the best solution to be adopted.

As a second point, the offer of machinery is still limited and those on the market are not flexible enough to obtain good results in a relatively large range of possible applications. A strong effort should be made by machinery producers in order to really push this technology.

Finally, capital investment and processing costs must be carefully considered. Vacuum plasma reactors are considerably more expensive than atmospheric ones and, at the present stage, they cannot be integrated into a continuous line. However, they are more controllable, flexible, adaptable to new productions and require much smaller amounts of chemicals. A fast pay-off of the investment costs is possible only if something completely new and well-accepted by the market is produced. Substitution of conventional finishing treatments with plasma treatments has much longer pay-off times, especially if water, energy and waste treatment costs are not exactly taken into account. In Table 11.3 a schematic comparison of the characteristics of plasma and conventional processes is reported.

It should also be considered that the textile productive chain is very complex and is made of a great number of extremely specialised small operators. Penetration by completely new technologies is always difficult and takes place on a large scale only when they have proven clearly their advantages in respect to traditional ones.

11.5 Industrial applications

Despite the difficulties and obstacles described above, other aspects are pushing in favour of plasma. The great advances of the last decades in the field of the science of materials are now ready to enter into the field of textiles and it is already possible to envisage that, in the next ten years, the clothing–textile industry will undergo a dramatic revolution. Smart textiles, completely new fibres (nanofibres, etc.), and new textile applications in unexpected fields can be expected. Also, our way to consider clothing is going to change completely. Environmental aspects are going to play a more and more important role. Under these perspectives, plasma processes are certainly going to supersede many traditional finishing processes.

Actually, today, many companies, especially for technical and special applications, have already adopted plasma technologies and the interest in plasma is growing at a very fast rate. Following this increasing attention of the textile world, many machinery manufacturers are developing new plasma machines of various types, which will soon be on the market. It is easy, therefore, to envisage that, in the near future, plasma technologies will become commonplace in the textile-clothing chain. As far as the present

Table 11.3 Comparison of plasma and conventional processes

	Plasma	Conventional
Solvent	Dry	Water (or organic solvents)
Chemicals	Gases in limited amounts	Large amounts
Type of reactions	Very complex and not well known	Simple and well known
Energy consumption	Limited for atmospheric-pressure plasma. Greater for vacuum plasma	High
Temperature	Room temperature	High temperature
Type of treatment	Surface treatment (<10–20 nm); no modification of bulk properties	Mass treatment or surface treatment (>100 nm); often modifications of bulk properties
Substrates	The same equipment can be used on all textile materials under different operative conditions	Different textile materials require different processes
Type of process	Batch (vacuum plasma) Batch or continuous (atmospheric-pressure plasma)	Batch or continuous
Equipment	Complex and in evolution	Simple and very well known
Competency required	High specialisation	Standard
Investment costs	High for vacuum plasma; lower for atmospheric plasma	Wide range of costs depending on the type of process
Waste treatment costs	Extremely limited	High

situation is concerned, certainly it is not possible to give an exhaustive view of all the industrial applications already at work in the world. So, only a short survey, principally limited to the Italian experience, will be reported here.

Air, oxygen and nitrogen low-pressure plasmas are mainly used. Increasing adhesion of chemicals or polymers to fibres and providing fabrics with marked hydrophilic properties leaving all the other properties substantially unaltered are, by far, the most important applications. Industrial plasma pre-treatments are currently used for the following finishing processes in order to improve the properties, the quality, and the useful life of the final products and to reduce the amount of chemical substances needed to obtain a certain effect:

- hydrophobic or oleophobic finishing of Nomex fabrics
- hydrorepellent finishing for polyamide fabrics for skiwear
- antibacterial finishing for microfibre lining of shoes
- flame-retardant finishing for home textiles
- coupling of polyester fabrics and polymeric membranes for surgical wear
- coupling of polyester fabrics and polymers for industrial tapes.

Plasma treatments as real finishing steps are also increasingly used, as mentioned before, for improving hydrophilicity, water vapour transfer, and drying rate properties of fabrics, all characteristics that can ensure clothing with very high comfort levels. The principal examples are:

- cycling polyester knitwear
- knitted underwear
- lining fabrics for overalls of Formula 1 racing car drivers
- shirts for Formula 1 teams
- jackets for workwear
- cycling shoe lining fabrics
- polyester fabrics for surgical applications.

The above list is far from being complete and new items could be added everyday.

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11.7 References

Abidi N, Hequet E (2004), *J Appl Polym Sci*, 93, 145.
Abidi N, Hequet E (2005), *J Appl Polym Sci*, 98, 896.
Akovali G, Dilsiz N (1990), *Polymer Eng Sci*, **30**(8), 485.
Andreozzi L, Castelvetro V, Ciardelli G, Corsi L, Faetti M, Fatarella E, Zulli F (2005), *J Colloid Interface Sci*, 289, 455.
Barni R, Riccardi C, Selli E, Massafra M R, Marcandalli B, Orsini F, Poletti G, Meda L (2005), *Plasma Process Polym*, 2, 64.
Benerito R, Ward T, Soignet D, Hinojosa O (1981), *Text Res Journal*, 51, 224.
Bhat N V, Benjamin Y N (1999), *Text Res. Journal*, **69**(1), 38.
Blanchard E J, Graves E E, Reinhardt R M (1999), *Colourage Annual*, 55.
Cai Z, Qiu Y, Zhang C, Hwang Y, McCord M (2003), *Text Res Journal*, **73**(8), 670.
Chaivan P, Pasaja N, Boonyawan D, Suanpoot P, Vilaithong T (2005), *Surf Coat Tech*, 193, 356.
Charbonnier M, Alami M, Romand M (1996), *J Electrochem Soc*, **143**(2), 472.
Chen J (1991), *J Appl Polym Sci*, 42, 2035.

Chen J (1996), *J Appl Polym Sci*, 62, 1325.

Cruz-Barba L E, Manolache S, Denes F (2002), *Langmuir*, 18, 9393.

D'Agostino R, Cramarossa F, Benedictis S (1982), *Plasma Chem Plasma Process*, 2, 213.

Denes F *et al.*, (1997), *J Photopol Sci Techn*, **10**(1) 91–112.

Ganapathy R *et al.*, (1966), *J Photopolymer Sci Tech*, **9**(2), 181.

Goodman J (1960), *J Polym Sci*, 44, 551.

Hautojarvi J, Laaksonen S (2000), *Text Res Journal*, **70**(5), 100–107.

Hochart F, De Jaeger R, Levalois-Grützmacher J (2003), *Surf Coat Tech*, 165, 201.

Höcker H, Thomas H, Küsters A, Herrling J (1994), *Melliand Textilberichte*, 75, 506.

Höcker H (2002), *Pure App. Chem*, **74**(3), 423.

Holme, I (2000), *Proceedings of 10th International Wool Textile Research Conference*, Aachen.

Kamel M, Youssef B M, Shokry G M (1998), *J Soc Dyers Color*, 114, 101.

Kan C W, Chan K, Yuen C W M, Miao M H (1998), *J Mater Process Technol*, 83, 180.

Kang J, Sramadi M (2004), *AATCC Rev*, 4/11, 29.

Kim M S, Kang T J (2002), *Text Res Journal*, **72**(2), 113.

Kobayashi S, Wakida T, Niu S, Hazama S, Doi C, Sasaki Y (1995), *J Soc Dyers Color*, 111, 111.

Lee H *et al.*, (2001), *Surf Coat Tech*, 142–144, 468.

Liao J, Chen C, Wu Y, Weng C (2004), *Plasma Chem and Plasma Process*, **25**(3), 255.

Massafra M R, Colonna G M, Marcandalli B, Occhiello E (1996), *Proceedings of the 17th IFVTCC Congress*, June 6–7, Wien.

McCord M G, Hwang Y J, Qiu Y, Hughes L K, Bourham M A (2003), *J Appl Polym Sci*, 88, 2038.

Molina R, Erra P, Julià L, Bertran E (2003), *Text Res Journal*, **73**(11), 955.

Möller M (2006), *Proceedings of the 3rd International Conference of Textile Research Division*, Cairo.

Oh K W, Kim S H, Kim E A (2001), *J Appl Polym Sci*, 81, 684.

Öktem T, Ayham H, Seventekin N, Piskin E (1999), *J Soc Dyers Color*, 115, 274.

Okuno T, Yasuda T, Yasuda H (1992), *Text Res Journal*, **62**(8), 474.

Özdogan E, Saber R, Ayahn H, Seventekin N (2002), *J Soc Dyers Color*, 118, 100.

Park J, Henins I, Hermann H W (2000), *Appl Physics Letters*, 76, 288.

Raffaele-Addamo A, Riccardi C, Selli E, Barni R, Piselli M, Poletti G, Orsini F, Marcandalli B, Massafra M R, Meda L (2003), *Surf Coat Tech*, 174–175, 886.

Raffaele-Addamo A, Selli E, Barni R, Riccardi C, Orsini F, Poletti G, Meda L, Massafra M R, Marcandalli B (2006), *Appl Surf Sci*, 252, 2265–2275.

Rakowski W, Osella R, Demuth O (1996), *Proceedings of the 17th IFVTCC Congress*, June 6–7, Wien.

Ranger E C, Bento W C A, Kayama M E, Schreiner W H, Cruz N C (2003), *Surf Interface Anal*, 35, 179.

Riccardi C, Barni R, Fontanesi M, Marcandalli B, Massafra M, Selli E, Mazzone G (2001), *Plasma Sources Sci Technol*, 10, 92.

Sarmadi A M, Kwon Y A (1993), *Text Chem Color*, 93, 25.

Selli E, Mazzone G, Oliva C, Martini F, Riccardi C, Barni R, Marcandalli B, Massafra M R (2001a), *J Mater Chem*, 11, 1985.

Selli E, Riccardi C, Massafra M R, Marcandalli B (2001b), *Macromol Chem Phys*, 202, 1672.

Shi L (2000), *Reactive Funct Pol*, 45, 85.

Sigurdsson S, Shishoo R (1997), *J Appl Polym Sci*, 66, 1591.

Šimor M, Ráhel J, Černák M, Imahori Y, Štefečka M, Kando M (2003), *Surf Coat Tech*, 172, 1.

Sparavigna A (2002), *Recent Res Devel Applied Physics* 5, 203–222.

Stone jr R B, Barrett jr J R (1962), *Textile Bull*, 88, 65.

Tyan Y C, Liao J, Wu Y, Klauser R (2002), *Biomaterials*, 23, 67.

Tyan Y C, Liao J, Lin S P (2003), *J. Mater Sci Mater Med*, 14, 775.

Urbanczyk G W, Lipp-Symonowicz B, Kowalska S (1983), *Melliand Textilberichte*, 11, 838.

Wakida T, Takeda K, Tanaka I, Takagishi T (1989), *Text Res Journal*, 59, (49).

Ward T, Jung O, Benerito R (1979), *J Appl Polym Sci*, 23, 1987.

Yip J, Chan K, Sin K M, Lau K S (2002), *J Mat Proces Technol*, **123**(1), 5.

Yoon N S, Lim Y J, Tahara M, Takagishi T (1996), *Text Res Journal*, 66, 329.

Yuranova T, Rincon A G, Bozzi A, Parra S, Pulgarin C, Albers P, Kiwi J (2003), *J Photochem Photobiol A: Chemistry*, **161**(1), 27.

Zhang J, France P, Radomyselskiy A, Datta S, Zhao J, van Ooji W (2003), *J Appl Polym Sci*, 88, 1473.

Zubaidi H, Hirotsu T (1996), *J Appl Polym Sci*, 61, 1579.

12

Characterisation of plasma-treated textiles

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12.1 Surface reactions in plasma treatment

Plasmas are energetic sources of radiation and chemical species, having a complexity of interactions with their surroundings. It is clear that the intense plasmas produced with highly energetic sources at high pressures in almost any gaseous environment will emit copious amounts of ions and electrons, radicals and excited neutral species, photons (from UV to IR), as well as heating their surroundings to high temperatures, and thus can cause severe damage to many materials. Low-pressure, low-energy plasmas are more benign but are still capable of damaging some materials that are exposed to them, and are indeed widely used to erode (etch) solids. Between these extremes are a variety of plasmas giving various fluxes of species with various energies. The possible effects produced by plasmas on textiles therefore range from heating to UV degradation, and from electrical charging to chemical alteration. Selection of an appropriate plasma system for a desired effect and its subsequent optimisation therefore requires some means of measuring this effect, and preferably monitoring some correlated feature of the plasma in order to give reliable control over the effect. If the material is to be coated by a plasma interaction, then it may be possible merely to measure the coating thickness with time, but a more subtle alteration of the surface properties may be extremely difficult to measure *in situ*.

Characterising a plasma-treated surface might involve determining any or all of the following: surface topography, chemical composition, mechanical strength, reaction to the environment (e.g. liquids, ultraviolet radiation) and durability. Fibrous materials have at least two ‘dimensional scales’ for which these properties may be measured: those for individual fibres and those for the conglomerate as a whole. Such fabric properties as drape will depend on the behaviour of individual fibres as they interact with each other across the whole material. However, a localised measurement of surface properties, such as on a single fibre, may not indicate the overall behaviour of a group of fibres, alteration of whose behaviour may be the purpose of the plasma treatment. Similarly, there may be inhomogeneities in the treatment if the plasma or its active ingredients do not penetrate the fibre network beyond the uppermost exposed surface. Nonetheless, it has been shown that oxygen plasma etching of woven PET was not affected by the fabric texture (Kuvaldina, 2000).

12.1.1 Plasma emissions

To see the relative significance of these problems, we should now consider the emanations from plasmas, including radiation, charged and neutral species, and how these may affect the properties mentioned above.

The most obvious feature of a plasma is its luminosity, which can extend from microwaves to deep UV. However, the ordinary cold fluorescent light tube produces visible light by generating UV photons in a low pressure gas that are then absorbed by a fluorescent coating on the inner surface of the tube, emitting specific colours in the process. Plasma TVs operate by a similar mechanism. Although the electrons in this type of plasma are highly energetic (‘hot’), they do not transfer much heat to the surroundings because of their low mass: the gas molecules in this type of plasma have much lower energies (‘cold’) and so also carry little heat to the surroundings. High intensity arc discharge lamps operate at high gas pressure, and both electrons and ionised gas molecules are hot, so that the lamp envelope becomes very hot from the energy the gas transfers to it. Both hot and cold lamps can be designed as efficient UV sources. Therefore, if similar conditions are present in processing plasmas, the material being treated will receive a high flux of photons, especially as the shortest wavelengths are not filtered out by the presence of a glass envelope between plasma and material, as they are for fabric exposed to fluorescent light tubes. The energies carried by UV photons from plasmas in some pure gases and simple mixtures (e.g. Fozza, 1998) are similar to those of chemical bonds in materials: a photon with energy ~5 eV (wavelength of ~250 nm) has greater energy than the O—H bond (~460 kJ mole^{-1}) or the C—H bond (~420 kJ mole^{-1}). Even the visible emissions are similar in photon energy to C—C bond strengths. Polymers that are degraded by long-term exposure to UV may therefore be damaged to some extent even by brief exposure to the highly energetic photons produced in plasmas; the actual cross-section for photon absorption is small and so a high photon flux is generally required for a significant amount of C—C and C—H cleavage. The effect may be mitigated by down-stream processing. Note that UV radiation will penetrate further into a material than the other plasma emissions (ions, electrons, radicals, etc.).

The electric fields that create plasmas do so by generating free electrons. Whilst the electron flux does not convey significant thermal energy to surfaces that are exposed to plasma, electrons do carry kinetic energy and electrical charge that may affect the material. Electrons can excite, ionise or dissociate molecules, and may induce desorption of atoms or molecules if these are only loosely bound to the surface of a material. Electron interactions will decrease with exposure time for an insulator, as it becomes negatively charged, so that electron-induced desorption is more significant for metallic surfaces. Examples of this type of desorption include hydrogen and CO from metals and semiconductors. If a sample does become charged from exposure to plasma, the energy released by a subsequent electrostatic discharge may generate sufficient heat to damage the material.

The free electrons in a plasma may ionise the gas or vapour, or cause a diatomic or polyatomic gas or vapour to dissociate, or may just create excited species from it. It is the transitions of bound electrons in atoms or molecules from excited states to lower energy states that produce the radiation seen from plasmas. (Not all such transitions radiate energy.) Most chemical effects from plasma treatment arise from the excited neutral species. These may be diatomic radicals, such as OH, CF_x, NH_x, or atoms such as H, O, F, N or polyatomic species such as higher hydrocarbons or ozone. An oxygen plasma may contain a mixture of ions and neutrals, such as O, O^+ and O^-, O_2^+ and O_2^-, O_3, and other active species, but the ions will be in a minority in most plasma conditions. Ions are encouraged in plasma etching, for instance of semiconductors, because they provide a directional beam on the sample that leads to anisotropic etching, through a combination of circumstances. Ions can, of course, sputter or ablate the surface layer by transferring kinetic energy to it. Compared with neutral species, ions may enhance the surface reaction kinetics. Thus the electrons and other species colliding with the surface of the material can create free radicals on the surface that will interact with the gaseous species to alter the surface of the material.

Although it is usually considered that the feedstock gas is the source of reactive species for plasma treatment of materials, there may be by-products from surface reactions that are vaporised and then either supplement or reduce the intended surface effect (e.g. oxygen plasma on wool can redeposit etched material if over-done: Molina, 2004). Almost inversely, it is possible for feedstock species to be implanted into the surface, even if these are chemically inactive: argon, in particular, is known to become embedded into some materials from plasmas, for instance during argon ion sputtering of another material from a solid target with the intention of coating the surface with this material alone. If these are ions, they may generate more damage in the material than would uncharged species.

12.1.2 Surface reactions

It is not commonly known which of these entities is responsible for altering any particular property of the material, and combinations of them are likely to be involved in many cases. Since a plasma is such an active soup of ingredients it is difficult to distinguish the influence of, say, the radicals from that of the neutrals, except in well-characterised cases. Although it is straightforward to monitor a particular wavelength of emission that may be known to arise from a particular electronic transition in a certain molecule (e.g. the strong green Swan band emission at 516 nm that comes from C_2 or the blue emission from CH or CH^+), the active ingredient in a particular plasma process may not have a radiative transition (e.g. CH_3 does not emit). Thus a plasma process for adding a carbonaceous layer may be controllable through an optical emission monitor if the process involves CH or C_2, but not if it relies on CH_3 unless some correlation has been proven first. If carbon-related emission is seen in a plasma when there are no carbon-containing gases, then this would indicate degradation of a carbon-containing fabric or the removal of carbon contamination from the surface, which is likely in energetic oxygen-containing plasmas.

Plasma deposition of a coating involves not only supplying the requisite mix of elements to the surface of the material, but also ensuring that it has active sites where these elements can bond. Attachment will occur by a balance of adsorption and desorption, often determined by the substrate temperature in physical vapour deposition, followed by surface diffusion and reaction. Each step will be affected by the plasma, and trouble-shooting an unsuccessful procedure by post-characterisation of the coating should attempt to discover which of these steps was ineffective. For instance, the balance of ions and radicals will affect the uniformity, structure and composition of the coating: the ion flux modifies the number of dangling bonds and the across-surface diffusion, and radicals can attach to dangling bonds or insert into the surface (Chang and Coburn, 2003). Complete characterisation of plasma deposition may require a chemical kinetics model, and for this the rates of the different processes and competing reactions must be known.

A frequent application of plasma treatment is to chemically functionalise the surface of organic materials, often by addition of OH, NH, CO, COOH, CH_x or CF_x groups. These can provide attachments for adhesives, biochemicals, or cells, without modifying the underlying structure of the material. The plasma abstracts hydrogen or breaks into the typical organic backbone without vaporising it into oligomers or monomers. Unless sufficient radicals are provided to attach to the break, it may cross-link with adjacent broken molecules. Over-exposing a polymeric fabric will risk damaging the surface so much that it is converted into short chains and vaporises. Plasmas containing oxygen or CF are known to alter the surface morphology of some fabrics (e.g. polyester: Sarmadi, 1993; polyaniline–Nylon 6: Kyung Wha Oh, 2001; carbon fibre–PEEK composites: Jang, 2004) but successful treatments can still be produced on many fabrics if they are not over-exposed (e.g. cotton copolymerised with vinyl groups: Abidi, 2004; wool keratin fibres: Molina, 2003).

With the increasing interest in atmospheric pressure plasmas for textile and polymer treatment (e.g. for surface cleaning, surface energy modification, or texturing), it should be recognised that, in contrast to low-pressure plasmas, these systems are likely to have a lower concentration of ions, lower numbers of highly energetic species and a smaller flux of UV photons, but may heat up the substrates more (Shenton and Stevens, 2001). On the other hand, at these higher pressures, the plasma should be more able to penetrate the fabric interstices (M Simor *et al.*, 2003, De Geyter *et al.*, 2006). De Geyter and coworkers showed that medium-pressure dielectric barrier discharge plasmas in air do indeed penetrate into non-woven polyester at higher pressures, but the active species must diffuse through the fabric from a plasma existing above the surface at somewhat lower pressures: in both cases, the fabric's surface energy was increased by oxidation. Fluorocarbon plasma generated by a cascade arc torch has also been shown to penetrate into PET non-woven fabric (Krentsel, 2003).

These contrasting examples of the plasma influence on fabrics demonstrate the potential difficulty in determining the 'active ingredient' from post-treatment characterisation of the fabric.

12.2 Techniques for characterisation of plasma-treated textiles

The field of surface engineering has been growing in the last 2–3 decades, primarily as sophistication of surface treatments and their potential for providing enhanced functionality to near surface regions has improved. Modification of surfaces while maintaining bulk material properties has obvious attractions in engineering applications across a wide range of materials from metals to ceramics to polymers. The current chapter is related to the plasma treatment of textiles – a surface modification methodology which has the potential to change functional characteristics such as wettability (Lai *et al.*, 2006), biocompatibility (Nuutinen *et al.*, 2003), strength (Sun *et al.*, 2006), surface reflectivity (Kaless *et al.*, 2005) and dyeability (Costa *et al.*, 2006) – these changes being induced by modification of a range of physical (e.g hardness, modulus), chemical (e.g. bonding) and topographical (e.g. roughness) properties.

Surface treatments of metals and other engineering materials are normally conducted with the intention that the bulk material properties are left intact. In some surface treatments, as a result of desired chemical changes there can be resulting physical changes and *vice versa*. Plasma treatment of textiles is known to induce chemical changes in the near surface regions and these can be due to incorporation of species in the surface or due to surface melting and resolidification – often these occur at conditions away from equilibrium. Characterisation of plasma-treated textiles requires techniques that will assess the above properties in the near surface region. 'Near surface' is a general description for the treated layer and, as will be described in this chapter, the analysis depth for various techniques defines '*near surface*'. The techniques for surface analysis will be divided into two main categories – those that assess physical and topographical properties and those that assess chemical properties.

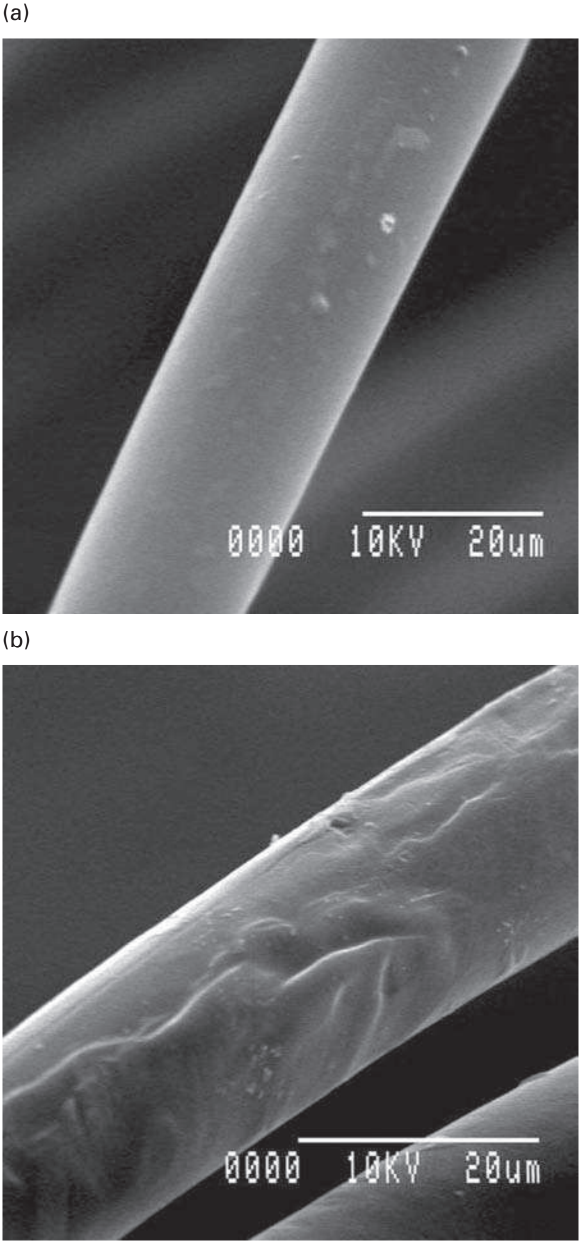
12.2.1 Physical and topographical

Scanning electron microscopy

The scanning electron microscope (SEM) was developed in the 1930s and brought about a different way of imaging solids (Knoll, 1935). By 1965, the first commercial instruments were in general use and this represented a revolution in microscopy. Using electrons to focus, it has the benefit of providing a great depth of field as well as extremely high resolution images at magnification levels of in excess of ×10 000. The SEM has been extensively used in analysis of the surface characteristics of plasma-treated textile fibres (Figure 12.1(a) and (b)) and woven materials. The information obtained from SEM is normally qualitative, simply providing an image of the surface at extremely high magnification. However, some software can be used to determine quantitative surface properties such as average roughness (R_a), rms roughness (R_{rms}) and fractal parameters.

A two-stage surface treatment process to graft acrylic acid functional groups on to plasma-modified poly(ethylene terephthalate)/polyethylene (PET/PE) was used by Chen and Chiang (2006) to increase biocompatibility. The post-test analysis involved examination of the fibroblast cell density on the fibre surface, detail that is routinely achievable with SEM. The curvature of the fibre surface and the cells adhered to the surface are clearly shown without loss of focus. There are numerous examples in the literature where SEM has been used to characterise surfaces treated by plasma processes; some recent examples are papers by Liu *et al.* (2006) on acrylic fibres, Lin *et al.* (2006) on nylon fabrics and on polyester fabrics by Costa *et al.* (2006).

A very important development in SEM came in the 1990s when the first environmental SEM was developed. This was an important technological advance in the area of polymer science, given the restrictions in SEM for



12.1 (a) SEM image of untreated PP fibre (b) SEM image of introgen treated PP fibre. (Courtesy of J. Warren, Heriot-Watt University.)

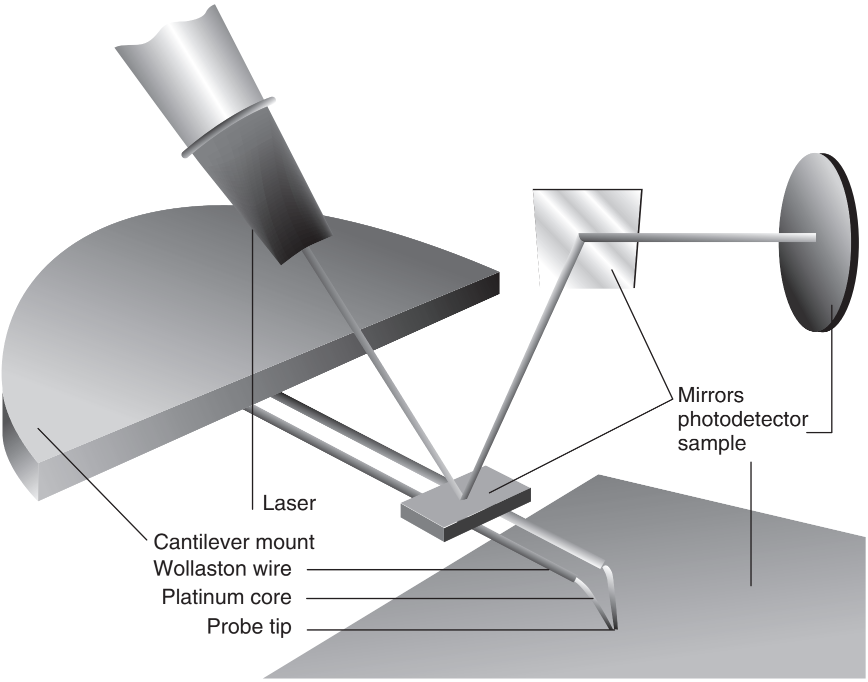
analysis of non-conducting samples. For examination of polymers using SEM, there is a need to apply a very thin sputtered layer of a metallic coating (normally gold) to provide a path for the discharge of electrons. Without this, the surface 'charges' and the image quality is extremely poor. With the introduction of ESEM, the need for coating was reduced, and sometimes eliminated, since the accelerating voltage could be reduced. The ESEM operates at much higher pressures than conventional SEM, which also brings benefits in terms of the ability to conduct experiments *in situ*. In the area of plasma treatment of textiles, the potential for observing the changes in the surface wettability by measurements *in situ* was realised by Hocker, 2002.

Atomic force microscopy

The development of the scanning tunneling microscope in 1981 earned Binnig and Rohrer the Nobel prize for physics. Scanning tunneling microscopy is one of the family of scanning probe microscopies (SPM) of which atomic force microscopy (AFM) is by far the most commonly used for analysis of plasma-treated textiles. Based on a relatively simple concept, the AFM has been partly responsible for the nano-revolution in materials science. Figure 12.2 shows the arrangement of the AFM. It comprises a scanning probe, with a tip (which is typically Si_3N_4) at the end of a cantilever. The probe is made to scan in the very near surface region (in the van der Waals forces) of a surface and an intricate control system enables the tip to follow the contours of the surface in great detail. Imaging of individual atoms has been possible, although in most applications this level of resolution is not normally required.

The AFM and other variants of the scanning probe techniques which emerged in parallel, or have been derived from, AFM have enabled unprecedented levels of detail to be reached on numerous surfaces across many fields of science. One major benefit of the AFM is the ability to image surfaces without the need for any complicated surface treatment process. It is a technique that can be used in air, and also imaging can be done in water, which makes it of particular usefulness in studies where the effect of liquids on surface structure (e.g. by swelling) are assessed. Crossley *et al.*, 2000 reported changes in the near-surface mechanical properties of wool when exposed to solvent cleaning by using high resolution force–distance (F–d) curves. These curves essentially enable the cantilever deflection on approaching and coming into contact with the surface, to be measured, hence giving a quantitative measure of the resistance to deflection.

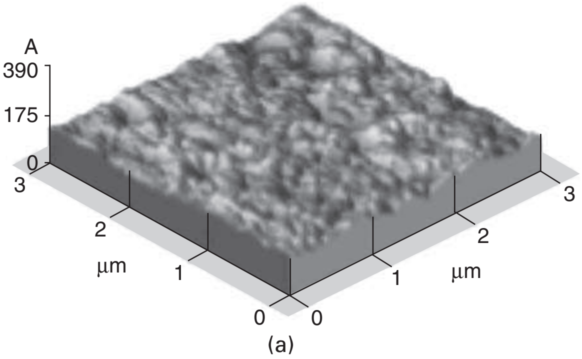
In fibre science several papers making use of the AFM have been published to date. These have concentrated on wool (Titcombe *et al.*, 1997; Jovancic and Jocic, 1998; Parbhu *et al.*, 1999; Crossley *et al.*, 2000),



12.2 Schematic representation of the Atomic Force Microscope.

polypropylene (Leijala and Hautojarvi, 1998; Hautojarvi and Leijala, 1999; Hautojarvi and Niemi, 2000; De Rovere *et al.*, 2000); polyethylene (Magonov *et al.*, 1991; Magonov *et al.*, 1993); carbon (Dilsiz and Wightman, 1999); Kevlar (Li *et al.*, 1993; Rebouillat *et al.*, 1997, 1999; Graham *et al.*, 2000); and various composite fibres such as nylon or polypropylene reinforced with carbon or aramid fibres (Klein *et al.*, 1996; Vancso *et al.*, 1997; Wu *et al.*, 1998). The surface properties of a textile fibre play a fundamental role in governing some key technical properties, and these properties are, to a large extent, related to the processing conditions (Rebouillat *et al.*, 1997). SPM offers the potential to probe surface characteristics at a level not previously achievable and, as such, it is likely that existing structural models will be confirmed or changed as the technique sees more application in textile characterisation.

In a recent paper by Kwon *et al.*, 2006 the hydrophobicity of PP films was altered by plasma treatment in argon and in a mixed Ar/O_2 atmosphere. The AFM was used to quantify the change in surface roughness of the treated surface as well as provide high resolution images showing the topography (Figure 12.3). The AFM has therefore been used in numerous studies to assess the topographical and physical changes in structure as a result of plasma treatment. In other areas of surface engineering, the AFM has been



12.3 AFM contact mode scanning image of the Ar-plasma treated surface of PP film (Kwon *et al.,* 2006).

used to quantitatively assess the near-surface mechanical properties. The AFM can be used to perform what are referred to as force–distance curves, which are essentially a type of indentation experiment at ultra-low loads. The cantilever tip is made to approach the surface at a given rate and then it contacts the surface. As it contacts the surface, the cantilever deflects and this deflection is recorded as a function of the tip position relative to the surface. To date, this has not been used in assessment of plasma-treated textiles as far as the authors are aware, yet there is potential to access very localised changes in surface hardness and also in surface chemistry as the adhesion force of the tip to the treated surface varies.

12.2.2 Chemical

X-ray photoelectron spectroscopy (XPS)

XPS is a very powerful surface analysis technique in which chemical states can be determined in near surface regions. Near surface in XPS can be as localised as the top 1–2 nm of the surface, and chemical characterisation as a function of depth is achievable through an etching processes (using argon ion bombardment). XPS is an ultra-high vacuum (UHV) technique and so the normal restrictions that this imposes apply. However, the analysis of plasma-treated textiles has yielded a wealth of very useful information relating to the chemical changes that induce functionality changes (e.g. wettability). In a recent paper by Liu *et al.* (2006), the plasma treatment of acrylic fibres and the mechanism by which anti-static properties were induced were reported and this work relied heavily on a detailed analysis using XPS. Amide and carboxyl hydrophilic groups were identified on the surface. Oxidation pathways were shown to occur at the cyanogen and ester groups on the polymer backbone. This study represents an example of a fully quantitative analysis of XPS, where curve-fitting procedures were used to fully identify the chemical species. In many other works (e.g. Su *et al.*, 2006), XPS is used to qualitatively show the change in chemical state through a shift in binding energy – in this paper the changes in C 1s, N 1s and O 1s were reported without full deconvolution of the peaks.

Fourier transform infrared (FT-IR)

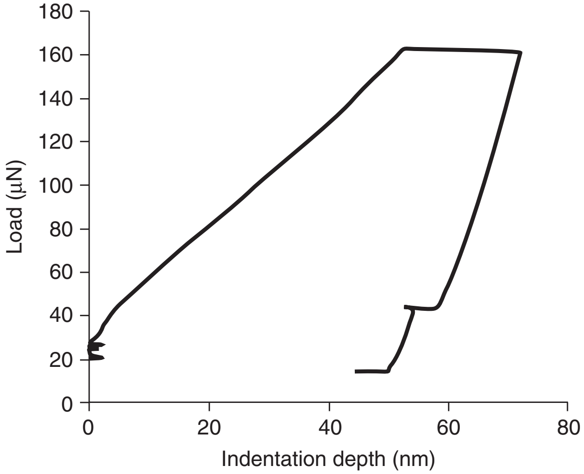
FT-IR is often used alongside XPS to provide a comprehensive analysis of how the surface of the polymer is changed as a result of plasma treatment. The vibrational spectroscopy enables important information on the C=C, C—O bonds to be determined and, in addition, the presence of important functional groups such as —OH, COO—, —OOH, —COOH, which can provide hydrophilic functionality at the surface (Cheng *et al.*, 2006). These groups have a fingerprint wavelength, and determination of the FT-IR spectra enables the surface bonding characteristics to be determined. This complements the chemical speciation information from XPS.

12.3 Future trends – Nanoindentation

Although nanoindentation has emerged as a very prominent technique in materials science since *ca.* 1975, in particular in surface coating technology, it has not been adopted widely in textiles. The technique relies on an accurate loading and unloading cycle where the resulting deflection of a nanoscale tip is measured as it is loaded and released. In the paper by Gindl *et al.* (2006), it was used to measure the surface characteristics of regenerated cellulose fibres. The loading and unloading cycle is represented in Figure 12.4 and can be used to determine properties such as (i) elastic modulus (ii) yield strength (iii) normalised hardness. Given that plasma-treated surfaces have experienced a temperature cycle and often some chemical changes by integration of species at the surface, it is very likely that both the AFM, for measurement of local force–distance curves, and the nanoindenter have great potential in surface characterisation of plasma-treated textiles and it is likely that this will be seen in the next few years.

12.4 Surface characterisation challenges

It is apparent that a whole variety of physical and chemical techniques can be brought to bear on the comparison of textile samples before and after gas plasma treatments. The link between the advances in scientific understanding which are gained from application of these techniques, particularly in combination with one another, and the improvements in technological performance brought about by gas plasma treatments, have now to be



12.4 Load–displacement curve for cellulose fibres (Gindl *et al.*, 2006).

forged. Many technological requirements of textiles depend on their surface character, e.g. abrasion resistance, ease (or difficulty!) of wetting, and ease of incorporation of additives such as dyestuffs.

The advent of advanced microscopies, such as ESEM and SPM, has already considerably progressed our understanding of the effects of specific gas plasma treatments on particular types of textile. However, as with the study of any sample by microscopy, there is the problem of the scale of the targeted sample. Microscopies, such as electron and probe microscopies, focus on only a tiny area of sample, compared with the far larger areas used in actual applications. In particular, these areas, with possibly significant edge lengths, may well not be homogeneous. This sampling problem can, to some extent, be sometimes overcome by the use of a micro- or nano-probe with rapid deployment over any part of the sample.

Textiles present some unique problems as samples for investigation. Textile fibre surfaces are curved, a factor that can present problems with depth of focus in optical microscopy, and even in electron microscopy. In the case of SPM, it is essential that the tip of the cantilever be placed as close as possible to the top of the fibre curvature. For both electron and probe microscopies, examination of a textured fabric sample, e.g. at the junction of two fibres, requires even greater care.

The effect of a given gas plasma treatment on a particular type of fibre can vary according to its cross-section. As stated above, plasma treatments induce changes in the near surface regions of fibres, usually down to a particular depth. For thicker fibres, such as monofilaments (diameters of the order of 100 μm), this depth will represent only a tiny fraction of their cross-section. With much thinner fibres, however, the effect of the plasma treatment could begin to impact on the fibres' bulk properties. This problem would be especially apparent in nanofibres, although investigations into the plasma treatments of nanofibres are still in their infancy.

Some technological concerns about the plasma treatments of textiles relate to the longevity and durability of the resultant surface changes. However, whilst even quite subtle changes may occur in the character of the treated surfaces, these changes may have marked effects on the performance of the textile. This aspect is pertinent right across the spectrum of textile usage: from the finish of a garment to the biological compliance of a medical device implanted in the body. For example, in the treatment of polypropylene fibre with oxygen plasma, a random copolymer of oxidised and unchanged units may result at the fibre surface (Gross *et al.*, 1994). The layer rearranges itself, however, depending on the medium with which the fibre is in contact, in order to minimise the free energy at the interface. The changes effected by plasma treatments in polypropylene, polyester and polyamide fibres may also be gradually eroded over a period of time (Radu *et al.*, 2000).

12.5 References

1. Abidi N & Hequet E (2004), *J Applied Polymer Science*, **93**: 145–154.
2. Chang J P & Coburn J W (2003), *J Vac Sci Technol (A)*, **21**: S145–S151.
3. Chen J P, Chiang Y-P (2006), Surface modification of non-woven fabric by DC pulsed plasma treatment and graft polymerisation with acrylic acid, *J Membrane Science*, **270**: 212–220.
4. Costa T H C, Feitor M C, Alves C, Freire P B, de Bezerra C M (2006), Effects of gas composition during plasma modification of polyester fabrics, *Journal of Materials Processing Technology*, in press.
5. Crossley J A A, Gibson C T, Mapledoram L D, Huson M G, Myhra S, Pham D K, Sofield C J, Turner P S, Watson G S (2000), Atomic force microscopy analysis of wool fibre surfaces in air and under water, *Micron*, **31**(6): 659–667.
6. De Geyter N, Morent R, Leys C (2006), *Plasma Sources Sci Technol*, **15**: 78–84.
7. De Rovere A, Shambaugh R L and O'Rear E A (2000), Investigation of gravity-spun, melt-spun, and melt-blown polypropylene fibers using atomic force microscopy. *Journal of Applied Polymer Science*, **77**(9): 1921–1937.
8. Dilsiz N and Wightman J P (1999), Surface analysis of unsized and sized carbon fibers. *Carbon*, **37**(7): 1105–1114.
9. Fozza A C, Kruse A, Hollander A, Ricard A, Wertheimer M R (1998), *J Vac Sci Technol (A)*, **16**: 72–77.
10. Gindl W, Konnerth J, Schoberl T (2006), Nanoindentation of regenerated cellulose fibres, *Cellulose*, **13**: 1–7.
11. Graham J F, *et al.* (2000), Spatially resolved nanomechanical properties of Kevlar (R) fibers. *Polymer*, **41**(12): 4761–4764.

12. Gross Th, Lippitz A, Unger W E S, Friedrich J F and Woll Ch (1994), *Polymer*, **35**: 5590.
13. Hautojarvi J and Niemi H (2000), Surface morphologies of polypropylene fibers studied by atomic force microscopy. *Textile Research Journal*, **70**(9): 820–827.
14. Hautojarvi J and Leijala A (1999), A morphological study of melt-spun polypropylene filaments by atomic force microscopy. *Journal of Applied Polymer Science*, **74**(5): 1242–1249.
15. Hocker H (2002), Plasma treatment of textile fibers, *Pure Applied Chemistry*, **74**(3): 423–427.
16. Jang J & Kim H (2004), *Polymer Composites*, **18**: 125–132.
17. Jovancic P M and Jocic D M (1998), The use of scanning probe microscopy (SPM) in wool surface investigation, *Tekstilna Industrija*, **46**(1–2): 5–14.
18. Kaless A, Schulz U, Munzert P, Kaiser N (2005), *Surface and Coatings Technology*, **200**: 58–61.
19. Klein N, Marom G and Wachtel E (1996), Microstructure of Nylon 66 transcrystalline layers in carbon and aramid fibre reinforced composites. *Polymer*, **37**(24): 5493–5498.
20. Knoll M (1935), Aufladepotentiel und Sekundäremission elektronenbestrahlter Körper. *Z tech Phys*, **16**: 467–475.
21. Krentsel E, Yasuda H, Miyama M, Yasuda T (1995), *J Polymer Science Part A: Polymer Chemistry*, **33**: 2887–2892.
22. Kuvalinda E V, Rybkin V V, Titov V A, Ivanov A N (2000), *High Energy Chemistry*, **34**: 398–401.
23. Kwon O-J, Myung S W, Lee C-S, Choi H-S (2006), Comparison of the surface characteristics of polypropylene films treated by Ar and mixed gas (Ar/O_2) atmospheric pressure plasma, *Journal of Colloid and Interface Science*, **295**: 409–416.
24. Lai J, Sunderland R, Xue J, Yan S, Zhao W, Folkard M, Michael B D, Wang Y (2006), Study on the hydrophilicity of polymer surfaces improved by plasma treatment, *Applied Surface Science*, **252**: 3375–3379.
25. Leijala A and Hautojarvi J (1998), Characterizing spin finish layers on polypropylene fiber surfaces by means of scanning force microscopy techniques, *Textile Research Journal*, **68**(3): 193–202.
26. Li S F Y, McGhie A J and Tang S L (1993), Internal structure of Kevlar fibres by atomic force spectroscopy. *Polymer*, **34**: 4573–4575.
27. Lin L H, Wang C C, Chen C W, Chen K M, Water repellency and antibacterial activities of plasma treated cleavable silicone surfactants on nylon fabrics, *Surface and Coatings Technology*, in press.
28. Liu Y-C, Yan X, Lu N D (2006), Surface characteristics and antistatic mechanism of plasma treated acrylic fibers, *Applied Surface Science*, **252**: 2960–2966.
29. Magonov S N, *et al.* (1991), Atomic force microscopy on polymers and polymer related compounds.1. Cold-extruded polyethylene. *Polymer Bulletin*, 1991. **25**(6): 689–694.
30. Magonov S N, *et al.* (1993), Atomic force microscopy of gel-drawn ultrahigh molecular-weight polyethylene. *Macromolecules*, **26**(6): 1380–1386.
31. Molina R, Jovancic P, Jocic D, Bertran E, Erra P (2003), *Surface and Interface Analysis*, **35**: 128–135.

32. Molina R, Canal C, Bertran E, Tascon J M D, Erra P (2004), *Current Issues on Multidisciplinary Microscopy Research and Education*, 242.
33. Nuutinen J P, Clerc C, Tormala P (2003), Mechanical properties and in vitro degradation of self-reinforced radiopaque bioresorbable polylactide fibres, *J Biomat Sci-Polym*, **E 14**(7): 665–676.
34. Oh K W, Kim S H, Kim E A (2001), *J Applied Polymer Science*, **81**: 684–694.
35. Parbhu A N, Bryson W G and Lal R (1999), Disulfide bonds in the outer layer of keratin fibers confer higher mechanical rigidity: correlative nano-indentation and elasticity measurement with an AFM, *Biochemistry*, **38**(36): 11 755–11 761.
36. Radu C-D, Kiekens P and Verschuren J (2000), Surface modification of textiles by plasma treatments, in *Surface Characteristics of Fibres and Textiles* eds. C.M. Pastore and P. Kiekens, Marcel Dekker: 203–218.
37. Rebouillat, S, Donnet J-B and Tong Kuan W (1997), Surface microstructure of a Kevlar aramid fibre studied by direct atomic force microscopy. *Polymer*, **38**(9): 2245–2249.
38. Rebouillat S, Peng J C M and Donnet J-B (1999), Surface structure of Kevlar(R) fiber studied by atomic force microscopy and inverse gas chromatography. *Polymer*, **40**(26): 7341–7350.
39. Sarmadi A, Kwon Y A (1993), *Textile Chemist and Colorist*, **25**: 33–40.
40. Shenton M J & Stevens G C (2001), *J Phys D: Appl Phys*, **34**: 2761–2768.
41. Simor M, Rahel J , Cernak M, Imahori Y, Stefecka M, Kando M (2003), *Surface and Coatings Technology*, **172**: 1–6.
42. Su F-H, Zhang Z-Z, Guo F, Song H-J, Liu W-M, Tribological properties of the composites made of pure and plasma treated-Nomex fabrics, *Wear*, in press.
43. Sun D, Stylios G K (2006), Fabric surface properties affected by low temperature plasma treatment, *Journal of Materials Processing Technology*, in press.
44. Titcombe L A, Huson M G and Turner P S (1997), Imaging the internal cellular structure of Merino wool fibres using atomic force microscopy, *Micron*, **28**(1): 69–71.
45. Vancso G J, *et al.* (1997), AFM imaging of interfacial morphologies in carbon fiber reinforced isotactic polypropylene. *Colloid and Polymer Science*, **275**(2): 181–186.
46. Wu C M, Chen M and Karger-Kocsis J (1998), Transcrystallization in syndiotactic polypropylene induced by high-modulus carbon fibers. *Polymer Bulletin*, **41**(2): 239–245.

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