Answers

1. Introduction

1.1. Vegetable: timber, cotton, cork, sisal, hemp, straw, reed, cane, capok, rattan, etc. Animal: wool, silk, fur, mohair, horse-hair, intestine, down, ivory, horn, sponge, beeswax etc.

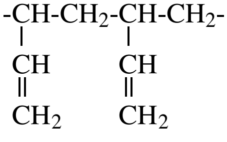
1.2. With half-synthetic plastics the polymer chain has been formed in a living tissue, but it has been chemically modified afterwards.
Cellophane is, after chemical modification, obtained from the cellulose in wood, just as paper (from cellulose and lignin), cellulose fibres (“rayon”), and cellulose plastics.
Leather is made from animal hides in a tanning process.
Natural rubber has to be vulcanised (with sulphur) to obtain a technically usable product.
Ebonite is also made from natural rubber, but with a much higher amount of sulphur; it belongs, therefore, to the family of thermosets.
Linen is obtained from flax after a chemical treatment (retting).
The boundaries between half-synthetic and natural polymers are sometimes vague.

1.3. In a cracking process the long, saturated, hydrocarbon chains in the crude oil are transformed into shorter ones, which, for lack of hydrogen atoms, contain double bonds, (-C=C-), which provide polymerisability.

1.4. When a diene, C=C-C=C, is polymerised, only one of the two double bonds is used; an unsaturated chain results, -C-C=C-C-, which offers the possibility of vulcanisation with sulphur.

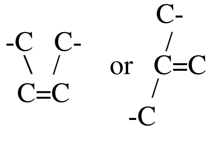
1.5. *a.* 1.4-polybutadiene, $-CH_2-CH=CH-CH_2-$

b. 1.2- of 3.4-polybutadiene,



$-CH(CH=CH_2)-CH_2-CH(CH=CH_2)-CH_2-$

in which under a. two different structures, cis and trans can be formed.



1.6. Ethylene-propylene copolymers, and also polyisobutylene, are rubbers with saturated chains, which cannot be vulcanised with sulphur. They are, therefore, copolymerised with a small amount of diene: EP with a diene in a sidegroup (e.g. dicyclopentadiene), PIB with isoprene (IIR = isobutylene-isoprene rubber = butyl rubber).

1.7. *a*. Polycondensation is possible with saturated monomers, e.g. a diol with a bifunctional carbon acid, by ester formation on two sides. In this reaction a small molecule, e.g. water is also formed.
b. After ring opening of saturated monomers these can also polymerise (e.g. caprolactam to PA-6).

1.8. *a*. By a reaction between tri-functional and bi-functional components, such as with the formation of phenol-formaldehyde or a polyurethane from glycerol and di-isocyanate.
b. By cross-linking polymer chains containing double bonds: with rubbers using small amounts of sulphur; with unsaturated polyesters using (poly)styrene.

1.9. “Thermosets” are cured into networks at elevated temperature from small molecules or from single chains.
The name could suggest that thermosets become harder at temperature increase; on the contrary: they soften just as all polymers at their glass-rubber transition, though their stiffness remains much higher than that of a rubber.
Moreover: curing is not always carried out at a high temperature; also “cold-curing” resins are used (e.g. in two-component adhesives or in large ship decks).

1.10. In thermoplasts the parts of different chains are bound to each other by weak secondary bonds, which are broken at higher temperatures. In thermosets and vulcanised rubbers the chains are permanently linked by primary chemical bonds, which, also at higher T, do not allow flow.

1.11. Thermosets have a tight network; with rubbers it is much looser; the cross-links are just sufficient to connect all chains at a few points.

1.12. In thermoplastic rubbers the chains are not connected by primary bonds as is the case with sulphur-vulcanised rubbers, but by weaker secondary bonds (e.g. within a PS domain in SBS), which are loosened upon temperature increase).

1.13. Thermoplastic rubbers (TPE’s) show rubbery behaviour at ambient temperature because the rubber phase plays the dominant part. In thermoplastics the behaviour of the glassy phase or of the crystalline part is dominant.

1.14. – Thermoplasts: PE, PS, PVC, PP.
– Thermosets: PF, UP.
– Rubbers: SBR.

1.15. LDPE, HDPE and LLDPE. They differ in density: LDPE between 0.91 and 0.92, HDPE between 0.94 and 0.96, and LLDPE between 0.92 and 0.95 g/cm^3. Since the density reflects the crystallinity, they also differ considerably in stiffness, between as well as within types.

1.16. – thermoplasts: PS, TPS, SAN, ABS en ASA.
- Thermosets: UP (is cross-linked with styrene).
- Rubbers: SBR and SBS.

1.17. PTFE with its very high melting point (327 °C) can only be transformed into an end product as a powder in a sintering process, since as a melt it would degrade at the high temperatures involved in other processing operations. Other fluor polymers such as FEP, PVDF and EFTE are suitable for the usual processing techniques.

1.18. PI, polyimide, can be used short-time up to 500 °C. Related to PI are: polyetherimides, polyesterimides en polyamidimides.

1.19. *a*. a. Blends of polymers
b. Particle- and short fibre- reinforced polymers
c. Composites
d. Foams

1.20. *a*. Carbon black is added to thermoplasts to decrease the electric resistance, in particular to prevent electrostatic charge, and also to shield the polymer from light, thus preventing ultraviolet degradation. Carbon black is added to rubbers to increase strength and abrasion resistance,
b. Chalk is a reinforcing filler in thermoplasts and thermosets.
c. Glass fibres are added to thermoplasts and thermosets to increase stiffness and strength, more than particles do.
d. Plasticisers are added to a polymer to reduce the glass rubber transition temperature drastically (e.g. with PVC), so that the polymer behaves as a rubber at ambient temperature rather than as hard glassy thermoplast.
e. Mica is a reinforcing filler which, due to its platelet structure, increases the stiffness more than spherical particles do.
f. Accelerators are added to thermosets and rubbers to speed-up the curing or vulcanisation process to such an extent that an end product can be formed under optimal conditions.
g. Lubricants are sometimes used to reduced the friction resistance in a shaping process.
h. Sulphur is essential in the usual processing technology of rubbers; it brings about the formation of “cross-links”, which provide the necessary shape stability.
i. Pentane is a blowing agent, applied in a.o. PS, to form foam.

j. Wood flour is a cheap filler, which brings about some stiffening (e.g. in PVC), and which reduces the price.

k. Antioxidants can, in the first place, protect a polymer against degradation at the high temperatures during processing; in the second place they can (mostly different types) prevent chain rupture during long-term use at elevated temperatures.

l. SiC is a very hard filler, mostly used to increase the abrasion resistance of a polymer.

m. UV-stabilisers protect a polymer against chain break under the influence of the ultraviolet components of daylight, often in combination with pigments (e.g. with PP).

n. Anti-static agents bring about a very thin layer of a conducting (hydrophilic) substance at the surface of the product, which allows electric charges, resulting from friction or contact, to be dissipated quickly.

o. Rubber particles are blended into a brittle polymer to increase its impact strength, e.g. butadiene rubber in PS, etc.

2. Molecular composition

2.1. – C-atoms only, or also other ones such as N, O, S or Si,
- saturated or unsaturated chains
- simple chains or chains containing rings, even composite rings (examples in MT 2.1.1)

2.2. *a.* PE $-CH_2-CH_2-$
BR $-CH_2-CH=CH-CH_2$
polyacetylene $-CH=CH-CH=CH-$
POM $-CH_2-O-CH_2-O-$
b. PP, PVC, PS, PB, PAN.
c. PIB, PVDC, PVDF (see MT 2.1.2).

2.3. PE, $-CH_2-CH_2-$, monomer mass = 2C + 4H = 2 × 12 + 4 × 1 = 28 g/mole,
PS, $-CH_2-CH(C_6H_5)-$, monomer mass = 8C + 8H = 8 × 12 +8 × 1 = 104 g/mole;
PA-12, $-(CH_2)_{11}-CO-NH-$, monomer mass = 12C + O + N + 23H =
12 × 12 + 1 × 16 + 1 × 14 + 23 × 1 = 197 g/mole.
M(PE) = 500 × 28= 14,000 g/mole,
M(PS) = 500 × 104 = 52,000 g/mole
M(PA-12)= 500 × 197 = 98,500 g/mole.

-C-C-C-C-C- chains lie zig-zag shaped, with C-C distances of 0.154 nm and with an angle between the bonds of 109.5°. The contribution of a C-C link to the contour length is, therefore, 0.154 × sin 54.2° = 0.126 nm.

- for PE the stretched length is thus 1000 × 0.126 nm = 126 nm (since the monomer contains two C-atoms),

- for PS also 126 nm,
- for PA-12: 13 links (for simplicity taking the same length for CO-NH-), so 500 × 13 × 0.126 nm = 820 nm.

The calculation is only valid for strictly linear PE, without branches. As to PS, it holds only for the syndio-tactic structure, since otherwise the neighbouring phenyl rings prevent a stretched conformation. (MT 2.5).

2.4. In this case equal *numbers* (both 1) are mixed. The number fractions are both 1/2 and the number average is $\frac{1}{2} \times 80{,}000 + \frac{1}{2} \times 120{,}000 = 100{,}000$. The weight fractions are, respectively, 80/200 and 120/200 or 0.4 and 0.6, so that the weight average is: $0.4 \times 80{,}000 + 0.6 \times 120{,}000 = 104{,}000$.

2.5. $n_i = N_i/\Sigma N_i$ = number of the species i divided by the total number = number fraction, $w_i = n_i \cdot M_i/\Sigma n_i \cdot M_i$ = weight fraction, $z_i = w_i \cdot M_i/\Sigma \mathrm{w}_i \cdot M_i$ = z-fraction$\overline{M}_\mathrm{n} = \Sigma n_i \cdot M_i$, $\overline{M}_\mathrm{w} = \Sigma w_i \cdot M_i$, $\overline{M}_\mathrm{z} = \Sigma z_i \cdot M_i$, $\Sigma n_i = \Sigma w_i = \Sigma z_i = 1$ (all normalised).

2.6. $\overline{M}_\mathrm{n} = \Sigma n_i \cdot M_i$; $n_i = (w_i/M_i)/\Sigma(w_i/M_i)$,
$\overline{M}_\mathrm{n} = \Sigma((w_i/M_i)) \cdot \mathrm{M_i})/\Sigma(w_i/M_i)) = \Sigma \mathrm{w_i}/\Sigma(w_i/M_i)) = 1/\Sigma(w_i/M_i))$

2.7. $\overline{M}_\mathrm{w} = \Sigma w_i \cdot M_i$; $w_i = (n \cdot M_i)/\Sigma(n_i \cdot M_i) = n_i \cdot M_i \overline{M}_\mathrm{n}$; $M_\mathrm{w} = (\Sigma n_i \cdot M_\mathrm{i}^2)/\overline{M}_\mathrm{n}$;
$\overline{M}_\mathrm{w} \cdot \overline{M}_\mathrm{n} = \Sigma n_i \cdot M_\mathrm{i}^2$.

2.8. $M_z = \Sigma z_i \cdot M_i$; $z_i = (w_i \cdot M_i)/\Sigma(w_i \cdot M_i) = w_i \cdot M_i \overline{M}_\mathrm{w}$; $\overline{M}_\mathrm{z} = (\Sigma w_i \cdot M_{i\mathrm{i}}^2)/\overline{M}_\mathrm{w}$;
$\overline{M}_\mathrm{z} \cdot \overline{M}_\mathrm{w} = \Sigma w_i \cdot M_{i\mathrm{i}}^2$.

2.9. *a*. In a mono-disperse polymer all chains are equally long (exception). Then $\overline{M}_\mathrm{n} = \overline{M}_\mathrm{w} = \overline{M}_\mathrm{z}$ etc..

b. The degree of dispersion or heterogeneity index, D, is defined as $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$,, and is, therefore, D = 1 for a mono-disperse polymer.

2.10. The chains break in a statistical way, by which shorter ones of various lengths are formed. The molar mass distribution is broadened in the direction of the low-molecular side.

2.11. In the blend every $(w_i)_A$ is replaced by: $w_A \cdot (w_i)_A$ and every $(w_i)_\mathrm{B}$ by $w_B \cdot (w_i)_\mathrm{B}$. So $\overline{M}_\mathrm{w}$ of the blend is:

$$\begin{aligned} \overline{M}_\mathrm{w} &= \Sigma(w_A \cdot (w_i)_A \cdot (M_i)_A) + \Sigma(w_B \cdot (w_i)_\mathrm{B} \cdot (M_i)_\mathrm{B}) \\ &= w_A \cdot \Sigma(w_i)_\mathrm{A} \cdot (M_i)_\mathrm{A} + w_B \cdot \Sigma(w_i)_\mathrm{B} \cdot (M_i)_\mathrm{B} = w_A \cdot (\overline{M}_\mathrm{w})_\mathrm{A} + w_B \cdot (\overline{M}_\mathrm{w})_\mathrm{B} \end{aligned}$$

2.12. The number of chains in one gramme of polymer is $N/\overline{M}_\mathrm{n}$ (N = Avogadro number). One gramme of the mixture contains w_A grammes of A, w_B grammes of B and w_C grammes of C, so that:

$$N/\overline{M}_\mathrm{n} = w_A \cdot N/(\overline{M}_\mathrm{n})_\mathrm{A} + w_B \cdot N/(\overline{M}_\mathrm{n})_\mathrm{B} + w_C \cdot N/(\overline{M}_\mathrm{n})_\mathrm{C}$$

of $1/\overline{M}_n = w_A/(\overline{M}_n)_A + w_B/(\overline{M}_n)_B + w_C/(\overline{M}_n)_C$.
The $\overline{M}_n$ values of A, B and C are 10, 20 and 30 kg/mole respectively 10, 20 en 30 kg/mole; $w_A = w_B = 10/(20 + x)$, $w_C = x/(20 + x)$, $\overline{M}_n$ = 15 kg/mole, so:
$1/15 = 10/(20 + x)\cdot 10 + 10/(20 + x)\cdot 20 + x/(20 + x)\cdot 30$, which results in: $x = 5$.

2.13. $\overline{M}_z = \Sigma w_i M_i^2/\Sigma w_i M_i$ of $\Sigma w_i M_i^2/\overline{M}_w$. Further evaluation is analogous to 2.11 and results in: $\overline{M}_z\cdot\overline{M}_w = w_1\cdot(\overline{M}_z)_1\cdot(\overline{M}_w)_1 + w_2\cdot(\overline{M}_z)_2\cdot(\overline{M}_w)_2$. So: $\overline{M}_z$ = 154.5 kg/mole.

2.14. $0.382 = k\cdot(76{,}000)^a$; $0.91 = k\cdot(250{,}000)^a$; $2.21 = k\cdot(850{,}000)^a$; we can plot $\log[\eta]$ versus $\log M$ to determine the slope a; we can also consider ratios of $[\eta]$: $0.91/0.382 = (250/76)^a$; a = 0.729; $2.21/0.91 = (850/250)^a$; $a = 0.725$; $2.21/0.382 = (850/76)^a$; $a = 0.727$; on average $a = 0.727$. With $0.91 = k\cdot 250{,}000^{0.727}$ we find: $k = 10.8\cdot 10^{-5}$.

2.15. $w_A = 0.37$; $w_B = 0.18$; $w_C = 0.45$. $\overline{M}_w$ (in kg/mole) = $0.37\cdot 76 + 0.18\cdot 250 + 0.45\cdot 850 = 455.62$ = 455,620 g/mole.
$1/\overline{M}_n = 0.37/76 + 0.18/250 + 0.45/850$; $\overline{M}_n$ = 163.457 = 163,457 g/mole.

2.16.

c	t	$t - t_o$	$(t - t_o)/t_o$	$(t - t_o)t_o c = \eta_{red}$
0	95.0	0		
0.1	107.7	12.7	0.1337	1.337
0.2	121.4	26.4	0.2779	1.390
0.3	136.3	41.3	0.4347	1.449
0.4	152.8	57.8	0.6084	1.521

When we plot η_{red} against c, it is clear that extrapolation of η_{red} to leads to 1.30 dl/g, so $[\eta]$ = 1.30 dl/g. From Mark-Houwink it follows (see 2.14): $1.30 = 10.8\cdot 10^{-5}\cdot M^{0.727}$, from which $\overline{M}_v$ = 410,000 g/mole, indeed slightly below $\overline{M}_w$.

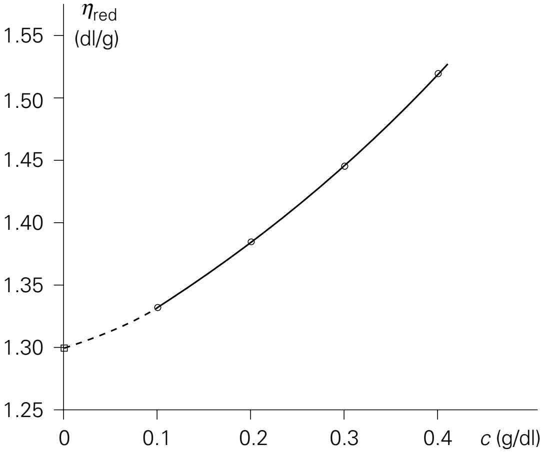


Figure A.1. Figure to the answer of problem 2.16.

2.17. With $\overline{M}_v = (\sum w_i M_i^a)^{1/a}$:
$\overline{M}_v = (0.37 \cdot 76{,}000^{0,727} + 0.18 \cdot 250{,}000^{0,727} + 0.45 \cdot 850{,}000^{0,727})^{1/0,727} = 409{,}340$, close enough to the answer on 2.16 .

2.18. We first calculate the various averages:
$w_1 = 0.10$, $w_2 = 0.18$, $w_3 = 0.25$, $w_4 = 0.17$,
$w_5 = 0.12$, $w_6 = 0.08$, $w_7 = 0.06$, $w_8 = 0.04$.
$M_1 = 15$, $M_2 = 27$, $M_3 = 39$, $M_4 = 56$, $M_5 = 78$, $M_6 = 104$, $M_7 = 120$, $M_8 = 153$.
$\overline{M}_n = 1/\sum(w_i/M_i)) = 1/(0.10/15 + 0.18/27 + \ldots) = 38.7$ kg/mole.
$\overline{M}_w = \sum(w_i M_i) = 0.10 \cdot 15 + 0.18 \cdot 27 + \ldots = 56.6$ kg/mole.
$\overline{M}_z = \sum(w_i M_i^2)/\overline{M}_w = (0.10 \cdot 15^2 + 0.18 \cdot 27^2 + \ldots)/56.6 = 78.8$ kg/mole.
$\overline{M}_{z+1} = \sum(w_i M_i^3)/\overline{M}_z \overline{M}_w = (0.10 \cdot 15^3 + 0.18 \cdot 27^3 + \ldots)/(78.8 \cdot 56.6) = 99.2$ kg/mole

a. The melt viscosity (zero-shear) is governed by $\overline{M}_w$, so as far as this is concerned the blend resembles fraction 4 .
b. The blend has a broader molar mass distribution; it behaves, therefore, stronger non- Newtonian (see MT 5.3.2) and flows better at high rates of shear.
c. The impact strength is mainly dependent on $\overline{M}_n$, so the blend resembles fraction 3.
d. The die-swell is a consequence of melt-elasticity which is governed by higher averages such as $\overline{M}_z$ and $\overline{M}_{z+1}$; here the fractions 5 and 6 are of importance.
e. The Young's modulus in the glassy state is independent of M.

2.19. In kg/mole: $M_1 = 60$, $M_2 = 600$,$\overline{M}_n = 1/\sum(w_i/M_I) = 1/((1 - w_2)/60 + w_2/600) = 100$, so $w_2 = 4/9$ and $w_1 = 5/9$; so 40 kg are needed.$\overline{M}_w = (5/9) \cdot 60 + (4/9) \cdot 600 = 300$ kg/mole = 300.000 g/mole.$\overline{M}_z = [(5/9) \cdot 60^2 + (4/9) \cdot 600^2)]/300 = 540$ kg/mole = 540.000 g/mole.

2.20. If we consider the coil as a sphere with a radius $r = (\langle r_o^2 \rangle)^{1/2} = 73.5$ nm then the volume of such a sphere is $V = (4/3)\pi r^3 = 1.663 \cdot 10^{-21}$ m^3. The mass m of the chain is $1000/6 \cdot 10^{23} = 1.667 \cdot 10^{-21}$ kg. The density, ρ, is then $m/V = 1.00$ kg/m^3. When we compare this with the density of PS, 1050 kg/m^3, then the coil is 1050 times 'diluted'

2.21. With $M = 10{,}000$ $\langle r_o^2 \rangle = n \cdot b^2$ is 100 times smaller; so the radius of the spherical coil is 10 times smaller and the volume V is 1000 times smaller. The chain mass is 100 times smaller, so the density, *r*, is 10 times greater. The 'dilution' is then 105 times.

2.22. In a tightest array of spheres the volume fraction is about 0.65; if we consider a maximum volume fraction of 0.3 to exclude all interaction effects, we find in the first case ($M = 10^6$) a maximum concentration of 0.3/1050 = 0.29 g/l = 0.028 g/dl (the densities of solvent and polymer considering as equal for convenience), and in the second case ten times 10 higher, so 0.28 g/dl.

2.23. The slope of η_{sp} versus c is greater as M is higher (at lower concentrations more effect of entanglements).

2.24. For convenience in kg/mole: $w_A \cdot 200 + (1 - w_A) \cdot 30 = 81$; $w_A = 0.3$; $w_B = 0.7$, so 300 kg of A and 700 kg of B.
$(\overline{M}_n)_A = 40$, $(\overline{M}_n)_B = 6$, $(\overline{M}_z)_A = 600$, $(\overline{M}_z)_B = 90$ kg/mole.
$1/\overline{M}_n = w_A/\overline{M}_n)_A + w_B/(\overline{M}_n)_B = 0.3/40 + 0.7/6$; $\overline{M}_n = 8.054 = 8054$ g/mole.
$\overline{M}_z = [w_A \cdot (\overline{M}_z)_A \cdot (\overline{M}_w)_A + w_B \cdot (\overline{M}_z)_B \cdot (\overline{M}_w)_B]/\overline{M}_w = (0.3 \cdot 600 \cdot 200 + 0.7 \cdot 90 \cdot 30)/81 = 467.8 = 467{,}800$ g/mole.
A directly produced batch would show: $\overline{M}_n = 81/5 = 16.2 = 16{,}200$ g/mole, and $\overline{M}_z = 3 \cdot 81 = 243 = 243{,}000$ g/mole. So the blend, though "on-spec" as regards its $\overline{M}_w$, has a two times lower $\overline{M}_n$ and a two times higher $\overline{M}_z$ as a user would expect. A blown bottle is, therefore, less resistant against stress-corrosion and impact failure at low temperatures. As a result of the stronger pronounced melt-elasticity the die-swell is higher , so the bottle is too thick and its manufacture requires more material!

2.25. *a.* a is usually between 0.5 and 1.0.
b. $\overline{M}_v$ is usually between $\overline{M}_n$ and $\overline{M}_w$, but closer to $\overline{M}_w$ as a approaches to a = 1.
c. When $a = 1, \overline{M}_v = \overline{M}_w$; when $a > 1$, $\overline{M}_v > \overline{M}_w$ (this can occur with very stiff chains).

2.26. When in solution, both substances will cause an increase in boiling point. At the same concentration this increase will, for a low-molecular substance, be considerably higher than for a polymer (readily a factor 100 of 1000 times greater), since the increase in boiling point is proportional to the number of molecules solved. An even simpler criterion is the viscosity of the solution: with a low-molecular substance hardly any change is noticed, where a polymer solution exhibits a significant increase in viscosity.

2.27. The number average degree of polymerisation $\overline{P}_n = 1/(1 - p)$, in which p is the degree of conversion. The weight average degree of polymerisation $\overline{P}_w = (1 + p)/(1 - p)$ (see MT § 2.2.2). so the heterogeneity index $\overline{M}_w/\overline{M}_n = \overline{P}_w/\overline{P}_n = 1 + p$, close to 2.

2.28. *a.* $HO\text{-}C_2H_4\text{-}OH = 62$; $HOOC\text{-}C_6H_4\text{-}COOH = 166$; the mass ratio is 62:166 = 1:2.68.
b. $HO\text{-}C_2H_4\text{-}OH + HOOC\text{-}C_6H_4\text{-}COOH = \text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-} + 2H_2O$; the polymer formed is polyethylene terephtalate (PETP).
c. P = number average degree of polymerisation, p = degree of conversion.
d. The molar mass of one unit is 192 (= 166 + 62 – 2·18), so 40.000/192 = $1/(1 - p)$ and $p = 0.9952$. $\overline{M}_w$ is $192 \cdot (1 + p)/(1 - p) = 79{,}800$ g/mole, nearly twice $\overline{M}_n$.

e. Growing chains can close to rings; small acid or basic contamination can terminate chain growth, etc.

2.29. With anionic polymerisation ("living polymers") all chains start at the same time and they grow at the same rate until the monomer is exhausted; the chains are, therefore, equally long.

2.30. $\overline{M}_n$: ebulliometry (boiling point increase); measurement of end group concentration (both for relatively low molar masses); osmometry for higher, but not too high molar masses.
$\overline{M}_w$: light scattering.
$\overline{M}_z$: sedimentation in solution by ultracentrifugeing.
Further: see MT 2.2.3.

2.31.

c (g/dl)	t (sec)	$(t - t_o)t_o$	$(t - t_o)/t_oc$ (dl/g)
0	100		
0.05	106.25	0.0625	1.25
0.1	115	0.15	1.5
0.15	126.25	0.2625	1.75
0.2	140	0.40	2.0

In this oversimplified case the limit for c = 0 can easily be determined without drawing a graph: $[\eta] = 1{,}0$ dl/g.

2.32. $[\eta] = k{\cdot}M^a$, so:

$$\begin{aligned} 0.5 &= k{\cdot}(5{\cdot}10^4)^a && (1)\\ 2 &= k{\cdot}(8{\cdot}10^5)^a && (2)\\ 1 &= k{\cdot}(x)^a && (3) \end{aligned}$$

From (1) and (2) it follows: $4 = 16^a$, so $a = 0.5$, and from (3) and (1): $(x/5{\cdot}10^4)^{0.5} = 2$ so $x = 200{,}000$.

2.33. a is already known ($a = 0.5$); k follows e.g. from: $0.5 = k{\cdot}(5{\cdot}10^4)^{0.5}$, so $k = 22.36 \cdot 10^{-4}$.

2.34. *a*. $\overline{M}_n = 1/(0.98/20.000 + 0.02/200) = 6{,}711$
$\overline{M}_w = 0.98{\cdot}20{,}000 + 0.02{\cdot}200 = 19{,}604$
$\overline{M}_z = (0.98{\cdot}20{,}000^2 + 0.02{\cdot}200^2)/19{,}604 = 19.996$
so: very strong effect on $\overline{M}_n$, small effect on $\overline{M}_w$, and hardly any effect on $\overline{M}_z$.

b. Here it is easier in kg/mole:
$\overline{M}_n = 1/(0.98/20 + 0.02/2000) = 20{,}4 = 20{,}400$ g/mol
$\overline{M}_w = 0.98{\cdot}20 + 0.02{\cdot}2000 = 59{,}6 = 59{,}600$ g/mol
$\overline{M}_z = (0.98{\cdot}20^2 + 0.02{\cdot}2000^2)/59{,}6 = 138{,}490 = 1.384{,}900$ g/mol
so: hardly any influence on $\overline{M}_n$, considerable effect on $\overline{M}_w$, very large effect on $\overline{M}_z$.

2.35. We calculate Π/c, for convenience first in mm/(g/dl):

c (g/dl)	Π (mm)	Π/c
0.12	6.50	54.2
0.18	9.94	55.2
0.25	14.05	56.2
0.33	18.8	57.0
0.45	26.6	59.1

Now we plot Π/c versus c. Extrapolation to c = 0 gives 52.8 mm/(g/dl). 1mm fluid pressure = $\rho g h$ = 903 kg/m^3·9.81 m/sec^2·10^{-3} m = 46.7 Pa and 1 g/dl = 10 kg/m^3. It follows that: Π/c = 46.77 m^2/sec^2. This equals RT/$\overline{M}_n$ = 8.314·298/$\overline{M}_n$, so $\overline{M}_n$ = 52.97 kg/mole or 52,970 g/mole.

2.36. Measurements of osmotic pressure provide an absolute determination (without calibration) of the number-average molar mass. This is independent of the type of solvent; for each solvent the extrapolation to zero concentration results in the same value: Π/c = RT/$\overline{M}_n$. With viscosimetry the determination of M is not absolute; dependent on the solvent and the temperature one finds a value for the intrinsic viscosity, [η], which is not unique but which has to be calibrated.

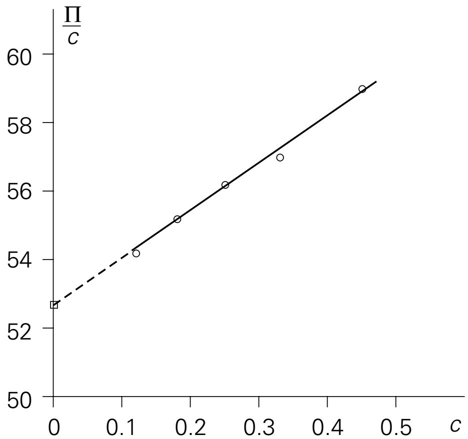


Figure A.2. Figure to the answer of problem 2.35.

2.37. The increase of viscosity from a certain concentration becomes more pronounced with increasing M (see Mark-Houwink), but the osmotic pressure is inversely proportional to the molar mass.

2.38. with p = 0.99, $\overline{P}_n$ = 1/(1 – p)= 100, with p = 0.995,$\overline{P}_n$ = 200. The mass of the unit link is: (-CO-(CH$_2$)$_4$-CO-NH-(CH$_2$)$_6$-NH-) = 12·12 + 2·14 + 2·16 + 22·1 = 226 g/mole. For A, therefore:$\overline{M}_n$ = 100·226 = 22,600 g/mole, for B: $\overline{M}_n$ = 200·226 =

45,200 mole. The weight-average degree of polymerisation is $\overline{P}_w = (1 + p)/(1 - p) =$ 199 for A and 399 for B. So the weight average molar masses are 199·226 = 44,970 (for A) and 399·226 = 90,170 (for B). (end groups disregarded for convenience).

2.39. $w_A = 0.3$; $w_B = 0.7$: $(\overline{M}_w)_A = 44{,}970$; $(\overline{M}_w)_B = 90{,}170$;
$\overline{M}_n = 1/(0.3/22.600 + 0.7/45{,}200) = 34{,}770$ g/mole (see 2.12),
$\overline{M}_w = 0.3{\cdot}44{,}970 + 0.7{\cdot}90{,}170 = 76{,}610$ g/mole,

2.40. We can measure $\eta_{rel} = \eta/\eta_o$ or $\eta_{sp} = (\eta - \eta_o)/\eta_o$ at a single concentration c (from the run times t_o and t),and calculate $\eta_{red} = (\eta - \eta_o)/\eta_o c$. η_{rel} or η_{sp} are in itself already convenient data to rank polymers of the same kind after their molar mass. If a quantitative estimation of $[\eta]$ is desired, then these values can be corrected by the known general dependence of η_{red} on c.

2.41. The principle of Problem 2.40 is the basis of the *k*-value, used with PVC. A measurement of the running time through a viscometer at a fixed concentration, compared with that of the pure solvent, results, after a standard calculation, in the k-value, which is, for that polymer, a simple index for the molecular mass. In technological terms one knows that a PVC with $k = 70$ (high M) does not flow easily, but it provides excellent end-use properties, e.g. in the long-term strength of pipes. In injection moulding a better flow is required; then a PVC with $k = 55$ is more appropriate.

2.42. The melt flow index is a useful indication of the molar mass, since it is a reciprocal measure of the melt viscosity η. η depends very strongly on: η (:) $\overline{M}_w^{3,4}$, (doubling of $\overline{M}_w$ results in a 10.6 times higher η!). This relation is valid for the 'zero-shear' viscosity; the melt index is measured at a shear stress where the non-Newtonian behaviour, and thus the width of the molar mass distribution, is already playing a part (see MT § 5.3.2). The melt index is a functional measure for the molar mass, because for a producer of end products the processability is often of primary importance.

2.43. From the results of the light scattering experiments it follows that A and B have the same $\overline{M}_w$. The viscosity average, $\overline{M}_v$, is for A higher than for B, and is thus closer to $\overline{M}_w$. A has, therefore, a narrower molar mass distribution and a higher $\overline{M}_n$. The osmotic pressure Π is therefore lower.

2.44. Large coils diffuse through the porous gel via the broadest channels, thus following the shortest way, and they arrive as the first at the end. Smaller coils are able to follow all side paths and have a longer travelling time.
The result of a GPC-measurement is a curve of w_i against M_i from which $\overline{M}_w$ can be calculated. Conversion to $w_i/M_i)$ against M_i and to $w_i{\cdot}M_i$ against M_i gives the possibility to calculate $\overline{M}_n$ and $\overline{M}_z$ as well.

2.45. – head-head and head-tail polymerisation in irregular sequences (exception).
- atactic instead of iso- or syndiotactic structure (example: PP).
- irregular branching (example: PE).
- with unsaturated chains: cis-, trans- and 1.2 configurations distributed at random (examples: BR and IR).
- with copolymers: random distribution of building blocks (examples: SBR and E/P).

2.46. Isotactic: all R-groups are at the same side of the main chain; syndiotactic: in alternating positions; atactic: randomly situated. All of this has to be considered in 3D space due to the tetraedric structure round a C-atom (see MT 2.3).

2.47. An atactic structure is in both cases not crystallisable. Atactic PP is because of its glass-rubber transition temperature (T_g = –15 °C) rubbery and technically of no use. Isotactic PP is able to crystallise and can, therefore, be used in practice. For PS atacticity is no objection; its properties as a glassy polymer are retained up to its T_g (95 °C).

2.48. – by a stiff main chain, e.g. with rings (example: aromatic polyamides).
- by big side groups (example: PS).

2.49. – strong interactions: dipole forces, e.g. in PVC (-Cl) and PMMA (-$COOCH_3$).
also: hydrogen bridges, e.g. in PA and PU (NH....OC).
- weak interactions: dispersion forces, e.g. in PE and PP.

2.50. cross link density = number of connected units / total number of units. Another measure is the molar mass between cross-links, M_c, The degree of cross-linking can be determined experimentally from the swelling in a solvent or from the E-modulus.
vernettingsdichtheid = aantal verbonden eenheden / totaal aantal eenheden.

2.51. Chemical cross linking is the formation of primary chemical bonds between chains, such as sulphur bridges (rubbers) or polystyrene bridges (UP), both between unsaturated chains. In saturated chains cross linking can be brought about after radical formation by irradiation or peroxides. Physical cross linking is based on secondary bonds (e.g. domains in thermoplastic elastomers) or entanglements.

3. Glassy state and glass-rubber transition

3.1. Similarities: Both are not able to crystallise because of their irregular molecular structure. Both will, therefore, reach the glassy condition upon cooling down from the liquid phase.

Differences: When a low-molecular glass is heated it will, at its T_g, immediately change into a liquid (though less abrupt as at a real melting point). A polymeric glass, however, first becomes rubbery as a result of chain entanglements. At a higher temperature (T_v) it passes very gradually into the fluid state.

3.2. All three quantities (V, H and S) show an upward jump at T_m upon heating (apart from "pathological" liquids such as water as regards V). At T_g there is, however, no jump, so $\Delta V = 0$, $\Delta H = 0$ and $\Delta S = 0$, but a bend, or a jump in their first derivatives. For V, H and S this means, respectively, jumps in the coefficient of expansion α, in the specific heat c and in the compressibility k.

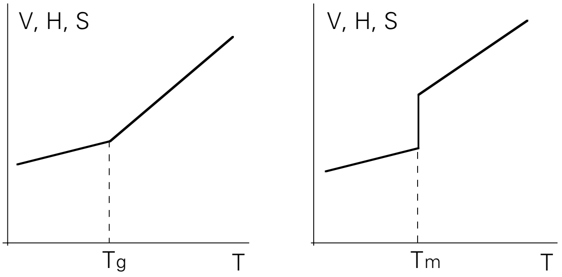


Figure A.3. Figure to the answer of problem 3.2.

3.3. Because of the many entanglements a long chain is still fixed at a number of points, so that only parts of the chain (of the order of 50 to 100 links) are free to move. At further temperature increase these entanglements are also loosened, so that the polymer is able to flow (T_v region).

3.4. – Large side groups increase the distance between the chains and thus decrease the interaction forces and, consequently, the T_g; example: polyhexene-1 (see also Question 3.6).

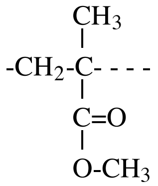
- Plasticisers, added in a sufficient quantity, also remove the chains from each other. Example: PVC with di-octylphtalate, where the polar attraction forces are strongly reduced and T_g may be lowered by more than 100 °C.

3.5. A thermodynamically defined transition is a transition between two equilibrium states. The glassy state is, however, never in thermodynamic equilibrium; it is subjected to volume-retardation (rearrangement of chain segments) up to unimaginably long times. The glass-rubber transition should, therefore, be considered as a freezing-in phenomenon, governed by kinetics.

3.6. The side group in polyhexene-1 is a straight and flexible C_4 chain; the one in PMP is, however, branched and rigid. Both side groups act as spacers between the chains, thus tending to a lower T_g, but with PMP this effect is overcompensated by the chain stiffening as a result of the rigid side group.

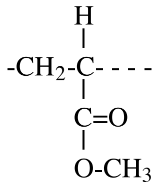
3.7. The difference between the T_g's of PP and PE is caused by the much greater chain stiffness of PP as a result of the hindered rotation round the C-C bonds in the main chain; the CH_3-groups are in the way.
In PVC rotation is hindered in a similar way (the Cl atoms are of about the same size as the methyl groups). The Cl atoms, bound to the main chain, are strong electrical dipoles and they exert much larger attraction forces on each other than the methyl groups in PP, which are subjected to the much weaker dispersion forces only.
The same reasoning applies to the series BR, IR, CR. Here again we see an increasing T_g. Now, however, less methyl- and Cl-groups are present, namely one on four C-atoms instead of one on two. There is no effect of the double bond: this is present in all three polymers in the same way.

3.8. PMMA:
(110 °C)



$-CH_2-C(CH_3)(C{=}O)(O-CH_3)----$

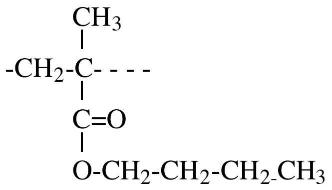
p.methylacrylate:
(5 °C)



$-CH_2-C(H)(C{=}O)(O-CH_3)----$

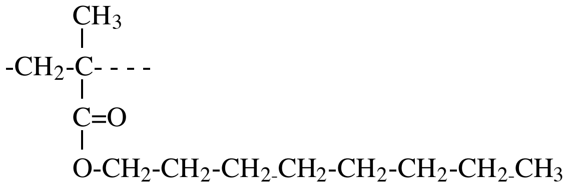
This difference in T_g is a result of the enormous effect of the methyl group at the main chain on the chain flexibility.

poly(n-butylmethacrylate):
(25 °C)



$-CH_2-C(CH_3)(C{=}O)(O-CH_2-CH_2-CH_2-CH_3)----$

poly(n-octylmethacrylate):
(–20 °C)



$-CH_2-C(CH_3)(C{=}O)(O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3)----$

Increase of the length of the (flexible) side group increases the distance between the chains and lowers T_g. Moreover, the polarity of the side group decreases, with the same effect on T_g.

3.9. – The polymer may show a secondary transition in the glassy region as a result of small movements of parts of the chain or side groups (example: PC).
- A blend of two incompatible polymers also shows two transitions: the T_g's of both components (example: TPS, toughened PS, PS + BR).
- A block copolymer tends to segregation; then there are two phases present with each their own T_g (example: SBS).

3.10. SBR is a random copolymer of styrene and butadiene, and it has, therefore, a T_g between that of poly-butadiene (–90 °C) and polystyrene (+95 °C). Its position depends on the S/B ratio, which is chosen in such a way that the polymer can function optimally as a technical rubber for tyres.

SBS is a three-block copolymer of styrene and butadiene. Incompatibility of PS and poly-butadiene (BR) causes segregation of the chain parts: a two-phase system results in which PS and BR each have their own individuality and their own T_g. The fact that the highest T_g is lower than the T_g of normal PS, is a result of the relatively low molar mass of the PS chain ends. In general the effect of M on T_g is insignificant: $T_g = T_g^{\infty} - K/M$, but when K is, e.g. 10^5 and $M = 10{,}000$, T_g can be 10° lower.

3.11. With copolymers it is of importance whether a one-phase or a two-phase structure is formed (random- or block-copolymers). In a similar way we see with polymer blends two (extreme) cases: real blends of wholly compatible components, and dispersions of incompatible ones. In the first case, which seldom occurs (e.g. PS with PPE) we find a single T_g; in the second case two T_g's, namely those of the two components.

3.12. Since the glass-rubber transition is characterised by large chain parts becoming mobile (e.g. 50 monomer units), we can from a single T_g only conclude that the blend is homogeneous on that scale; at a smaller scale (of a few links) a two-phase system may still be present.

3.13. The glass transition is mainly governed by chain interactions and chain mobility. Cross-linking will hardly influence the interactions, but the mobility is hindered by the cross-links. T_g will, therefore, increase with increasing network density.

3.14. When a chain with $M = 200{,}000$ g/mole is linked to other chains at four points, the average molar mass between cross-links, M_c, amounts to 40,000. The mass of one unit is $4 \times 12 + 6 \times 1 = 54$ g/mole; so the number of units between cross-links is about 740. At the glass-rubber transition no whole chains obtain free mobility, as a result of the entanglements, but chain parts of 30 to 100 monomer units. The chemical cross-links, therefore, hardly contribute to the restriction in chain mobility; the increase in T_g will, therefore, be negligible.

3.15. Polyamides (nylons) can absorb water up to a few percent, which acts as a plasticiser (the distance between the chain segments is increased), so that T_g is lowered. T_g is, therefore, dependent on the environment (dry air, moist air or water). The extremes may differ by several tens of degrees.

4. Crystalline polymers

4.1. A polymer which is in principle crystallisable because of its regular chains, may crystallise too slowly to develop, under normal circumstances, a detectable degree of crystallinity. In such a case the kinetics play the major role.

4.2. PC and PPE (T_g 150 and 215 °C) would have melting points of, respectively:
3/2 (150 + 273) – 273 = 361 °C(asymmetric chain) and
2(215 + 273) – 273 = 703 °C (symmetric chain).
In both cases processing above T_m would lead to strong degradation.

Poly-isobutylene (PIB) is a very useful rubber because of its very low gas permeability. Co-polymerised with small amounts of isoprene (to enable vulcanisation with sulphur) to butyl rubber (IIR), it is the ideal rubber for inner tubes. If PIB would crystallise, it could not be used as a technical rubber! The same holds for the rubbers BR and IR.

4.3. Even with a high cis content the rate of crystallisation of BR and IR is so low, that generally speaking, no crystallisation occurs. However, upon stretching a few hundred percent, micro-crystallites are being formed spontaneously. These form extra cross-links between the chains, thus increasing the strength of the vulcanisate enormously. When the stress is released these crystallites disappear, so that the rubbery behaviour is completely restored. The same holds for butyl rubber, which has, apart from a few isoprene segments, a regular chain structure.

4.4. $T_m = \Delta H/\Delta S$, in which ΔH is the increase of enthalpy upon melting, and ΔS the entropy increase. ΔH is related to the chain interactions, ΔS to the chain flexibility.

4.5. T_m would be about 3/2 times T_g , so (3/2)×(273+85) – 273 = 264 °C. Processing of semi-crystalline PVC would only be possible above T_m ; however, the polymer cannot withstand such high temperatures.

4.6.

n	M	T_m (°C)	T_m (K)	1000/M	1000/T_m
8	114	–56.8	216.4	8.77	4.62
10	142	–29.7	243.5	7.04	4.11
15	212	10.0	283.2	4.72	3.53
20	282	36.8	310.0	3.55	3.23
32	450	69.7	342.9	2.22	2.92

After plotting 1000/T_m against 1000/M, and extrapolating the slightly curved line to 1000/M = 0, it appears that the first part of the curve can be represented by: 1000/T_m = 2.44 + 220/M.
So the melting point of PE with infinite chain length is 1000/2.44 = 410 K or 137 °C.
For T_m = 409 we find: M=37,000. With this low molar mass T_m appears to be only 1

°C lower than the maximum; so for practical grades the differences are tenths of a degree.

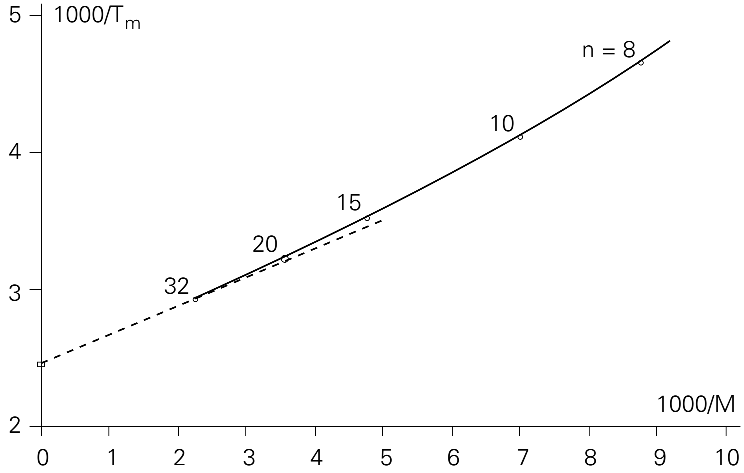


Figure A.4. Figure to the answer of problem 4.6

4.7. The coiled structure with entanglements does not allow complete crystallisation to occur. From very dilute solutions perfect crystals can be formed, in particular when the chain molecules are lying fully stretched and oriented. A technical example is the high-strength PE fibre: “Dyneema”.

4.8. The difference in T_m must be due to the previous history. The first sample has been quenched from the melt, and thus it is crystallised at a lower temperature, e.g. 130 °C. The crystallites are, therefore, smaller (more nuclei at a lower temperature) and less perfect than in the second sample, which was cooled more slowly and which crystallised at, e.g. 145 °C.

4.9. The lower the temperature of crystallisation, the lower the melting point of the best crystal will be, but also: the more imperfect crystallites are formed. The melting range of the sample with T_m = 161 °C is, therefore, broader.

4.10. PBTP has about the same chain structure as PETP, but has in the main chain four CH_2- groups instead of two with PETP. The chain is , therefore, more flexible, which results in a lower melting point.
PBTP crystallises considerably more rapidly than PETP. In an injection moulding process, where short cycle times are required, and thus rapid crystallisation during the rapid cooling in the mould, PBTP may, therefore, be preferred. PETP would stay amorphous, and, therefore, not usable above its T_g (69 °C).

4.11. Nucleating agents can be added to the polymer, which enhance the rate of crystallisation considerably. It is also possible to take the amorphous product from the mould and heat it for some time in an oven at some temperature above its T_g, so that it crystallises to form an acceptable end product.

4.12. Chain orientation enhances the rate of crystallisation, because every volume element in which a few chain parts lie parallel forms a nucleus. This is the case in fibre spinning, film stretching and bottle blowing.

4.13. In a (stereo-specific) rubber spontaneous crystallisation occurs under strain; here also small regions in which chain parts lie parallel, act as nuclei.These nuclei, which improve the strength considerably, do, however, not grow out into a continuous phase; they disappear upon stress release.

4.14. Nuclei with a radius r smaller than r_k are disrupted by the thermal motion; when $r > r_k$ the nuclei are stable and can grow. r_k is determined by the competition between the formation of new interface (interfacial energy has to be supplied) and the production of crystallisation heat. In the formula for r_k, $(T_m - T)$ is in the denominator, which indicates that with stronger super-cooling a nucleus can grow more easily.

4.15. The ratio of the crystallisation rates is 98/23 = 4.26, the ratio of the molar masses is 143/87 = 1.64. The ratio of the melt viscosities (which govern the crystal growth) amounts to $1.64^{3,4}$: 1 = 5.38. Apparently the rate of crystallisation is, next to the rate of nucleation, governed by the melt viscosity.

4.16. The T_g values of most of the polyamides are between 50 °C (PA-6 en PA -6.6) up to 82 °C (PA-4.6) (in ambient atmosphere a few tens of degrees lower due to moisture absorption). They, therefore, already lose their properties at some T increase. Crystallisation is, therefore, essential for technical applications
Amorphous polyamides should have a higher T_g (e.g. Gelon A 100 of General Electric with T_g = 130 °C) by the presence of aromatic rings in the main chain, and, moreover, an irregular chain structure (to prevent crystallisation), by the introduction of side groups.

4.17. With increasing n the -CO-NH- groups in the main chain are more and more “diluted” in the -CH_2- sequences; their effect decreases and T_g and T_m approach to the values of PE. The “zig-zag” effect is a matter of parity: the formation of hydrogen bridges is only possible if the groups are in the proper position.

4.18. - For a non-crystallisable polymer:
a. and b. equal
c. solidifies earlier
d. volume-retardation

- For a crystallisable polymer:
a. undercooling
b. melting range
c. more undercooling
d. post-crystallisation.

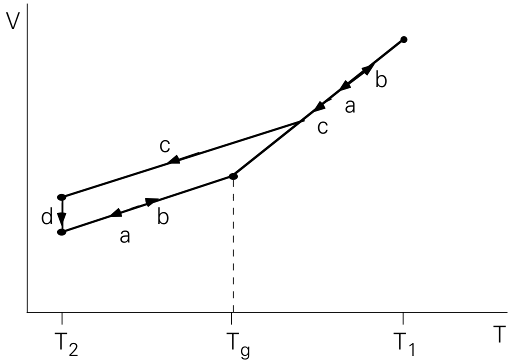


Figure A.5. Figure to the first part of the answer to problem 4.18.

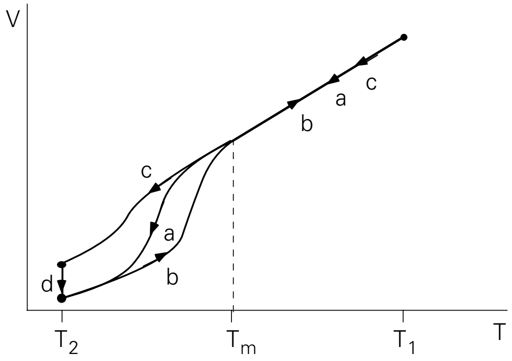


Figure A.6. Figure to the second part of the answer to problem 4.18.

4.19. *a.* T_g will certainly lie between 20 °C and 80 °C; probably between 30 en 70°.

b. PETP has an asymmetric chain, so $T_m = (3/2) \times T_g$, i.e. between (3/2)(273+30)-273 = 182 °C en (3/2)(273+70)-273 = 241 °C.

c. Above T_g crystallisation can occur in the rising branch of the curve for crystallisation rate vs temperature.

d. At T_m the rate of nucleus formation is zero; at T_g (and at T_m) the rate of crystal growth is zero ; between these two a maximum occurs (see MT § 4.3.2).

e. *See Figure A.7.*

f. *See Figure A.8.*

g. In the rapidly cooled mould of an injection moulding machine crystallisation proceeds too slowly and needs help from nucleating agents or annealing above T_g after moulding. See also problems 4.10, 4.11 and 4.12 .

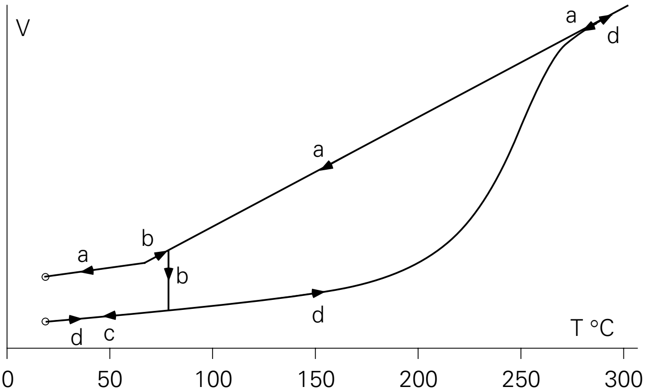


Figure A.7. Figure to the answer of problem 4.19e.

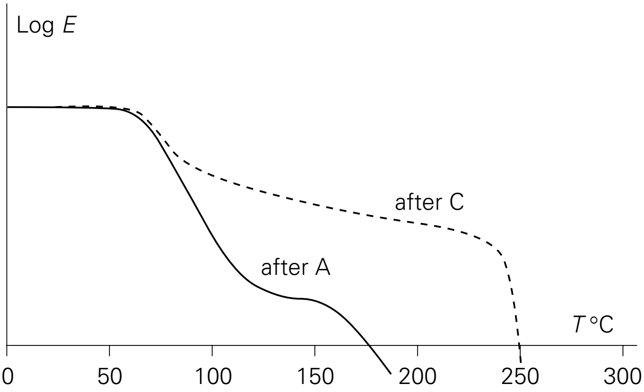


Figure A.8. Figure to the answer of problem 4.19f.

4.20. The volume of the unit cell is $0.740 \times 0.493 \times 0.253$ nm^3 = 9.230×10^{-29} m^3. When n CH_2- groups are present in such a cell, then the mass within the cell is $m = n \times 14$ g/mole, so $n\times14/\ 6\times10^{23}$ grammes = $14n/6\times10^{26}$ kg. The density is: $\rho = (14n\cdot10^{29})/(6\cdot10^{26}\cdot9.23) = 253\cdot n$ kg/m^3. n must be an integer and (must be slightly higher than the density of a near-linear PE (960 kg/m^3). Only $n = 4$ meets these conditions.

4.21. 1 cm^3 of the polymer has a mass of ρ grammes. It contains φ cm^3 of crystalline polymer with a mass of $\varphi\times \rho_c$ grammes and $(1-\varphi)$ cm^3 amorphous with a mass of $(1-\varphi) \times \rho_a$ gr. The total mass is $\varphi = (\rho - \rho_a)/(\rho_c - \rho_a)$..
1 gramme of the polymer has a volume of $1/\rho$ cm^3 and contains $(1/\rho) \times \varphi \times \rho_c$ grammes crystalline matter, so the crystalline mass fraction is $\psi = \varphi\cdot(\rho_c/\rho) = (\rho_c/\rho)\cdot(\rho - \rho_a)/(\rho_c - \rho_a)$.

4.22. The Avrami equation can be transformed into:

$$\log\left[-\ln(1 - \Delta V/\Delta V_\infty)\right] = \log c + \alpha\cdot\log t.$$

We can now construct the following table:

t	V	ΔV	$\lambda = \Delta V/\Delta V_\infty$	$1-\lambda$	$-\ln(1-\lambda)$
0	120.00	0	0	1	
500	119.16	0.84	0.084	0.916	0.0877
1000	114.97	5.03	0.503	0.497	0.6992
1500	110.94	9.06	0.906	0.094	2.364
2000	110.04	9.96	0.996	0.004	5.521
2500	110.00	10.00	1.000	0	

Plotting – $\ln(1-\lambda)$ against t, both on a log scale, indeed results in a straight line with slope 3, so $\alpha = 3$. c can e.g. be determined at $t = 1000$: $c = 7\cdot 10^{-10}$.

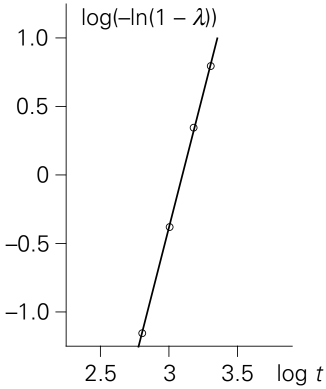


Figure A.9. Figure to the answer of problem 4.22.

b. α =3 can mean: three-dimensional crystal growth with heterogeneous nucleation of two-dimensional growth with homogeneous nucleation.

c. At 155 °C the exponent α will not change very much. c will, however, be considerably smaller as a result of much slower crystallisation.

d. The volume of the amorphous polymer is 120 mm^3; so the amorphous density is $\rho_a = 100/120$ g/cm^3. The density of the crystallised sample is $\rho = 100/110$ g/cm^3. With $\rho_c = 0.937$ g/cm^3 the crystalline volume fraction can be calculated: $\varphi_c = (\rho - \rho_a)/(\rho_c - \rho_a) = 0{,}73$.

4.23. From $\varphi_c = (\rho - \rho_a)/(\rho_c - \rho_a)$ it follows for LDPE: $\varphi_c = 0.38$ and for HDPE: $\varphi_c = 0{,}76$.

4.24. The cause can be found in the morphology of the polymer. The question is: is the amorphous phase continuous or the crystalline phase or both? This is further dealt with in Chapter 9.

4.25. A semi-crystalline polymer is a two-phase system; it consists of a crystalline phase and an amorphous phase, which, in most cases, have a different refractive index. Light is, therefore, deflected at each interface, which results in strong light scattering.

When, by exception, the refractive indices are equal (as in PMP), no light scattering occurs and the polymer is transparent.

When the crystallites are small enough (small in comparison with the wave length of the light), only minor scattering occurs. This can be achieved with nucleating agents, but also with chain orientation.

4.26. In a super-strong PE fibre the chains lie nearly completely stretched, and are thus loaded under optimal conditions. They must, however, transmit the mechanical stress on each other, which can only happen via transverse bonds. These are relatively weak binding forces (London-Van der Waals bonds), so the number of these bonds should be made as large as possible, which means very long chains.

4.27. For a semi-crystalline polymer the E-modulus shows between T_g and T_m (in which region it is already lower than below T_g), a rather strong decrease at increasing T, whereas with amorphous polymers, which are used below T_g, the stiffness is not much temperature dependent (apart from possible secondary transitions). The time dependency, or the creep, shows a similar behaviour.

As a matter of fact, this does not hold for semi-crystalline polymers far below their $T_{g.}$ (strong example: PEEK). The word "far" is here important, since creep proceeds up to very long times of loading, whereby T_g is lowered; the polymer can as it were creep towards its T_g!

4.28. Lyotropic LCP's are processed from a solution, thermotropic ones from the melt. In both cases the flow pattern provides the necessary orientation of the stiff chains.

Working with a solution is needed for polymers which above their melting point would degrade (example: aromatic polyamide fibres such as Kevlar and Twaron). For fibres the removal of the solvent is not too problematic. In e.g. injection moulding applications solvents cannot be used; here thermotropic LCP's have to be used. Since these would degrade during processing, they are "diluted" by copolymerisation (example: poly-hydroxy-benzoic acid - co - PETP)

4.29. The glass-rubber transition extends over a rather broad temperature region. T_g is, therefore, dependent on the chosen method of measurement and on the definition of the transition point. Moreover, T_g depends on the time scale of measurement. Though the melting point, T_m , is a well-defined quantity for an ideal crystal, melting also extends over a broad temperature region as a result of the differences in crystal perfection. The highest melting point found for a polymer depends on the quality of the "best" crystal, which depends on the regularity of the chain structure (compare

HDPE and LDPE) and on the rate at which the polymer has crystallised (so on the crystallisation temperature).

4.30. All three transitions are shown by a semi-crystalline thermoplastic with a chain length long enough to extend the rubbery region to above the melting point.

4.31. Only T_g and T_v are present in an amorphous thermoplastic and in a non-vulcanised rubber. A semi-crystalline thermoplast with short chains only shows T_g and T_m. In a (very exceptional) fully crystalline polymer T_g is not present

4.32. For vulcanised rubbers and for thermosets T_g is the only transition.

4.33. Between T_g and T_m the polymer contains a crystalline and an amorphous, rubbery phase. The rubbery phase is responsible for the high impact strength.

5. Rubbertoestand en vloeibare toestand

5.1. F is the free energy and is related to the Gibbs free enthalpy G, via $G = U + pV - TS = F + pV$. When F is used instead of G the work exerted on the environment by volume change is thus neglected. U is the internal energy, which increases when work is done to overcome interaction forces. T is the temperature in Kelvin. S is the entropy of the system, and is a measure for the probability of the state, or for the number of possibilities (conformations) at which the state can be realised.

5.2. When the length l is increased the force needed is:

$$K = \frac{\mathrm{d}F}{\mathrm{d}l} = \frac{\mathrm{d}U}{\mathrm{d}l} - T\frac{\mathrm{d}S}{\mathrm{d}l}$$

In the glassy state interaction forces have to be overcome, so $\mathrm{d}U/\mathrm{d}l$ is important. The entropy, however, hardly changes, since the chain conformations do not change at a small deformation. The force is, therefore: $K = \mathrm{d}U/\mathrm{d}l$.

In the rubbery state, on the contrary, the chain interactions are not or hardly active: they have, from T_g, been overcome by the thermal movement. The entropy, S, strongly depends on the deformation so the force is now given by: $K = -T \cdot \mathrm{d}S/\mathrm{d}l$.

5.3. The entropy change upon elongation is a matter of conformations, so purely topological, and is not influenced by temperature.

5.4. *a*. The molar mass of the isoprene unit (-CH_2-C.CH_3=CH-CH_2-) is 68 g/mole, of a half cross-link: 4×32 =128 g/mole. The mass fraction S is 0.005. When n isoprene units are between crosslinks, then $128 = 0.005 \times n \times 68$, so $n = 376$ and $M_c = 376 \times 68 = 25{,}600$ g/mole.

b. Substitute: $\rho = 910$ kg/m^3, $R = 8.31$ J/K.mole, $T = 298$ K, $M_c = 25.6$ kg/mole: $E =$

264.000 Pa.

c. *E* appears to be more than 5 times higher. Strain-induced crystallisation cannot be an explanation, for *E* is measured at very small strains. Deviation from ideal rubber-elastic behaviour gives a very small effect only. The explanation is the existence of physical entanglements, which are much more numerous than the S-bridges. (without vulcanisation also a value of nearly 1.5 MPa! is found!)

d. Entropy-elasticity dominates the behaviour: $T \times dS/dl$ is the important parameter. *S* is a matter of order/disorder: the number of possible conformations, The difference between conformation possibilities in strained and unstrained condition is greater as the freely moving chain part is longer; therefore M_c is in the denominator.

5.5. *a*. $M_c = 3\rho RT/E = 3 \times 910 \times 8.31 \times 293 \ / \ 2.2\times10^6 = 3.02$ kg/mole = 3020 g/mole. This amounts to 3020/54 = 56 monomer units. The use of proper units is very important ! In this case, i.e. for non-vulcanised rubber: M_c = molar mass between physical, temporary entanglements. Not the whole chain!

b. $E(100) = E(20) \times 373/293 = 2.8$ MPa, but: entanglements are loosened; there is a gradual transition to flow, so M_c increases and *E* decreases. The three deviations from ideal rubberelastic behaviour, mentioned in MT 5.1, are here, for non-vulcanised rubber, of much less importance.

5.6. *a*., *b*., *c*. See Figure A.10.

d. With light cross-linking T_g hardly increases, since the chemical cross-links are at much greater distances from each other than the physical entanglements. With tighter networks this is no longer the case, so that the chain mobility is hindered by the presence of the many cross-links and T_g is increased.

e. The same reasoning as above: In the formula $E = 3\rho RT/M_c$, the distance between cross-links, (expressed as molar mass M_c) is, with light vulcanisation, mainly governed by the physical entanglements. With higher degrees of cross-linking the distance between chemical bridges plays an increasing role, so that E increases.

f. For an ideal network *T* is in the numerator of the formula for *E*, so that *E* is proportional to the absolute temperature. The log *E* - *T* curve thus shows a positive slope (not a straight line because of the log-scale but slightly curved upward). In reality this simple picture is often disturbed by deviations from ideal rubber-elastic behaviour.

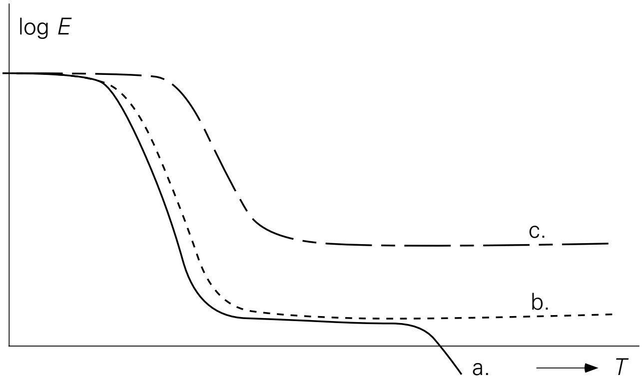


Figure A.10. Figure to the answer of problem 5.6.

5.7. When the rubber is heated from 253 K to 298 K, the E-modulus becomes 298/253 = 1.18 times higher. The wall stress in the balloon will increase by 18% and the diameter decreases to 20/1.18 = 17 cm. Gradually the air in the balloon will be heated up, and the pressure will increase proportionally to the absolute temperature. Eventually the old diameter of 20 cm will be reached.

5.8. First: Also in the rubbery condition flow will occur and in the fluid state the melt also shows elastic properties.

Secondly: the transition from rubber to flow is strongly dependent on the molar mass: this transition is governed by the unravelling of chain entanglements, which are, with long chains, much more numerous than with short ones.

Thirdly: the longer one takes the time to disentangle the coils, the easier this is performed. The time scale plays, therefore, also a large role. At short times a polymer may behave as a rubber, whereas it flows at longer times. (think e.g. of “silly puttee”).

5.9. *a.* en *b.*: see Figure A.11. A twice as high molar mass gives a $2^{3.4} = 10.6$ times higher zero-shear viscosity, in which the relevant average is M_w is (η (:) $M_w^{3,4}$) The whole curve is thus shifted upward by a factor 10 (one unit on the log scale). Broadening of the molar mass distribution shifts the curve to the left; the zero-shear viscosity does not change.

c. the “power-law” holds for the right-hand part of the curve, which often resembles a straight line. From $\tau = k\cdot(\dot{\gamma})^n$ it follows, together with $\tau = \dot{\gamma}\cdot\eta$: $\eta(:)\tau^{(1-1/n)}$. When $n = \frac{1}{2}$ $\eta(:)\tau^{-1}$, so on the log-log scale the slope is –1 (45° to the left).

d. In injection moulding shear stresses and shear rates are high, so that a broad distribution is beneficial for easy mould-filling. However, the high $\overline{M}_z$ may be responsible for high melt-elasticity resulting in frozen-in orientations and anisotropy.

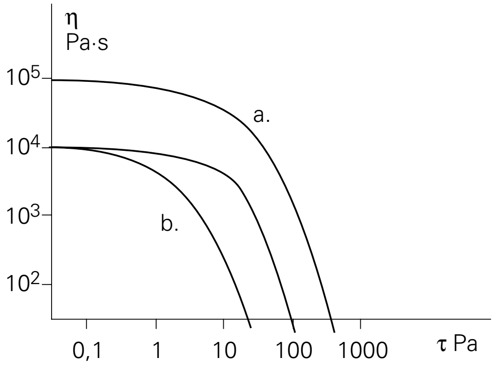


Figure A.11. Figure to the answer of problem 5.9.

With rotation moulding τ is very small; a narrow distribution may then be preferred, also because a higher M_n favours the impact strength etc. With film extrusion a broad distribution is advantageous for making very thin films and for the elastic effects (M_z) required in shrink films; a narrow distribution results in better tear strength and impact resistance (M_n).

5.10. In a plot of log η vs. log τ the curves are shifted vertically upon a change in M or in T. (see MT Figure 5.12). In such a plot the melt-index can also be indicated easily, since the m.i. is measured at a fixed stress.

5.11. *a*. The melt flow index is measured at a shear stress which may strongly differ from the one present in a processing operation. In particular with injection moulding the latter is much higher than the former.

b. By a higher value of the shear stress, so a greater force on the plunger, better agreement can be reached, e.g. instead of 2.16 kgf: 5 or 10 or even 21.6 kgf.

c. At e.g.10 kgf the ratio of the melt flow indices is higher than 10 /2.16 ; this ratio increases with increasing width of the molar mass distribution (non-Newtonian behaviour or 'shear-thinning').

5.12. An increasing melt-flow index signifies decreasing molar mass; with polymers made in the same process both $\overline{M}_w$ and $\overline{M}_n$ are lower. Since the impact strength is governed by $\overline{M}_n$, it decreases with increasing m.f.i. With a narrower MMD $\overline{M}_n$ is, however, higher than what would be expected on the basis of the m.f.i; therefore the impact strength is also higher.

5.13. A higher m.f.i. means a lower molar mass and a lower melt viscosity. The rate of crystallisation will then be higher, and a grade with a higher m.f.i. will crystallise better and reach a higher degree of crystallinity, thus a higher stiffness. For the grades with a narrower MMD one would expect, at the same m.f.i., a lower $\overline{M}_w$, so a lower zero-shear viscosity (see MT, Figure 5.14), which would result in a higher crystallinity and a higher stiffness. It is, however, the other way round. Possibly in the crystal growth process higher shear stresses and -strains are involved than under m.f.i. conditions; possibly other, unknown causes play a part.

5.14. Polyethylene crystallises much more rapidly than polypropylene; under usual cooling conditions PE will always reach its maximum possible crystallinity, irrespective of its chain length, contrary to PP. An exception is formed by the ultra-high-molecular PE (UHMWPE), in which the chains are exceptionally long ($M > 10^6$ g/mole), the viscosity exceptionally high and the crystallinity (also the density) slightly lower. However: super- strong PE -fibres are made from the longest possible chains, but the crystallinity is extremely high as a result of the near-perfect alignment of the chains.

5.15. *a*. “die-swell”. i.e. recoil of the elastic deformation of the melt after it leaves the die of an extruder;

b. “melt fracture”: the elastic strain may be so high that the material breaks; the product is distorted;

c. crystallisation: with a crystallisable polymer (e.g. a stereospecific rubber) the elastic strain may reach such high values that spontaneous orientation-induced crystallisation occurs, causing considerable trouble in the process (see MT Figure 5.15).

d. when the elastic deformations (chain orientations) are frozen in during cooling, an anisotropic end-product results, which shows different stiffness and strength in different directions. Also the refractive index may be dependent on the direction (bi-refrigence, which is of importance with e.g. compact discs).

6. Visco-elasticity

6.1. A Maxwell element shows an instantaneous elastic deformation and thereafter unlimited flow. For polymers in the solid condition the latter is not realistic. For a fluid polymer it is more relevant; moreover, the instantaneous elastic deformation is in accordance with the real behaviour: when the stress is released a polymer fluid shows an instantaneous recoil.

6.2. *a*. $\varepsilon_o = \sigma/E = 10^4/10^5 = 0.1 = 10\%$.

b. $\varepsilon = \varepsilon_o + \sigma \cdot t/\eta = 0.1 + 10^4 \cdot 500/10^7 = 0.6 = 60\%$.

c. σ relaxes between $t = 500$ and $t = 800$ sec with $\sigma = \sigma_0 \exp(-t/\tau)$, in which $\sigma_o = 10^4$, $t = 300$ sec and $\tau = \eta/E = 100$ sec, so $\sigma = 10^4 \cdot e^{-3} = 500$ Pa (e^3 is close to 20).

d. See Figure A.12.

e. - Non-linearity. - spectrum instead of single relaxation time

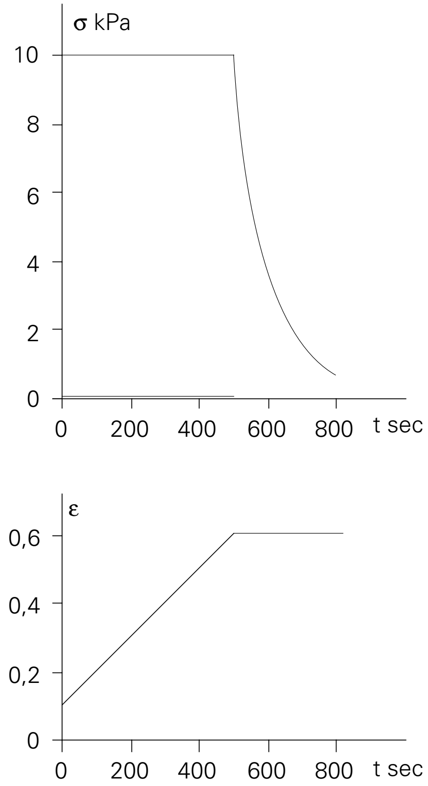


Figure A.12. Figure to the answer of problem 6.2

6.3. Evidently a fluid polymer cannot be considered; in the model the deformation approaches to a limit. For a solid polymer the model seems more appropriate, though is represents neither a spontaneous elastic deformation nor permanent flow. Therefore a combination of a Kelvin-Voigt element with a spring and with a dashpot in series is, in principle, more appropriate.

6.4. Cross-section of the bar = $A = 10^{-2} \cdot 10^{-3} = 10^{-5}$ m^2; the stress $\sigma = K/A = 600$ N/ 10^{-5} m$^2 = 60 \cdot 10^6$ N/m^2 = 60 MPa.

The strain is Δl (mm)/l (mm) = Δl(mm)/100, so for 1 mm strain is $\varepsilon = 0.01$.

a. The model shows instantaneous strain and retarded strain, and it can, therefore, in principle be represented by a spring E_1 in series with a Kelvin-Voigt element with E_2 and η.

b. From the instantaneous strain (2 mm) it follows: $\varepsilon = 0.02$. So E_1 is: $E_1 = \sigma/\varepsilon_o$ = 60/0.02 = 3000 MPa.

The limit of the strain is 8 mm, so $\varepsilon = 0.08$, of which the Kelvin-Voigt element accounts for 0.08 - 0.02 = 0.06 , so in $\varepsilon = \sigma/E_1 + (\sigma/E_2) \cdot (1 - \exp(-t/\tau))$ is σ/E_2 = 0.06, so $E_2 = \sigma/0.06$ = 60 MPa/0.06 = 1000 MPa.

At last the retardation time τ: at $t = 250$ sec ε = 7,5 mm = 0.075. Substitution:

$0.075 = 0.02 + 0.06 \cdot (1 - \exp(-250/\tau)$ results in: $0.055 = 0.06 \cdot (1 - \exp(-250/\tau))$; $\tau = 100$ sec $= \eta / E_2$, so $\eta = \tau \cdot E_2 = 100 \cdot 10^9 = 10^{11}$ Pa·s.

c. When the stress is released after 250 sec the strain on E_1 disappears instantaneously; so the total strain decreases from 7.5 to 5.5 mm. Thereafter the strain decreases as: $\varepsilon = 5.5 * \exp(-t/\tau)$, where t starts at 250 sec.

d. Non-linearity and spectrum rather than a single retardation time.

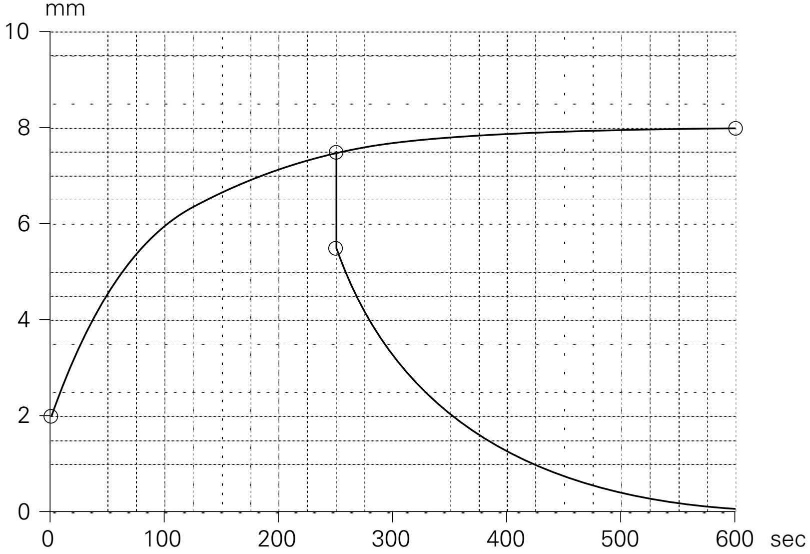


Figure A.13. Figure to the answer of problem 6.4.

6.5. *a.* $\varepsilon_o = \sigma / E_2 = (6 \cdot 10^6)/(3 \cdot 10^9) = 0.002 = 0.2\%$ (only the spring in series).

b. $\varepsilon(3 \cdot 10^6) = \varepsilon_o + \varepsilon_1 = 0.002 + (\sigma / E_1) \cdot (1 - e^{-t/\tau})$, $(\tau = \eta / E_1 = 10^6 \text{ sec}) = 0.002 + (6 \cdot 10^6)/(3 \cdot 10^8) \cdot (1 - e^{-3}) = 0.002 + 0.02 \cdot 0.95 = 0.021 = 2.1\%$

c. E_2 recoils: $\varepsilon = 2.1 - 0.2 = 1.9\%$.

d. The Kelvin element recoils with: $\varepsilon = 0.019 \cdot \exp(-3 \cdot 10^6/10^6) = 0.019 \cdot 0.05 = 0.095\%$.

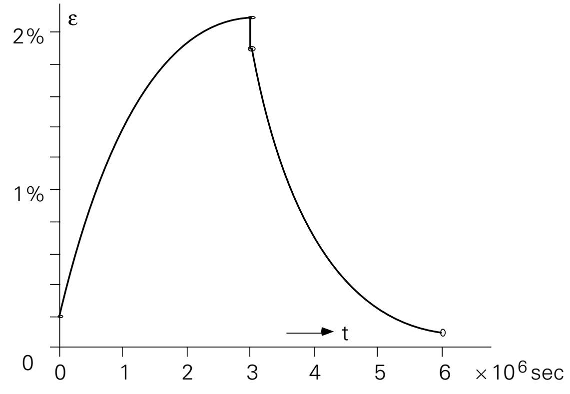


Figure A.14. Figure to the answer of problem 6.5.

6.6. The course of the strain can be described by superimposing the effects of the two stresses; the first one is σ, applied at $t = 0$, and continued after t_1; the second one is $-\sigma$, applied at $t = t_1$. We find then from $t = t_1$:

$\varepsilon = (\sigma/E_2) + (\sigma/E_1)\cdot(1 - \exp(-t/\tau)) - (\sigma/E_2) - (\sigma/E_1)\cdot(1 - \exp(-(t - t_1)/\tau) =$
$= (\sigma/E_1)\cdot\{\exp(-(t - t_1)/\tau) - \exp(-t/\tau)\} =$
$= (\sigma/E_1)\cdot\{1 - \exp(-t_1/\tau)\}\cdot\{\exp(-(t - t_1)/\tau)\} =$
$= \varepsilon(t_1) \cdot \exp(-(t - t_1)/\tau),$

in which $\varepsilon(t_1)$ is the strain at t_1 immediately after the release of the stress.

Without the superposition principle we find the same result : After taking away the stress the spring E_2 is unloaded and we keep the deformed Kelvin-Voigt element with a strain: $\varepsilon = (\sigma/E_1)\cdot(1 - \exp(-t_1/\tau)) = \varepsilon(t_1)$.

The spring E_1 now pulls back the Kelvin-Voigt element from $t = t_1$ with a stress σ, proportional to the remaining deformation ε: $\sigma = E_1\cdot\varepsilon(t - t_1)$.

The rate of deformation is given by the behaviour of the dashpot: $d\varepsilon/dt = -\sigma/\eta$ (negative, since the deformation decreases).

So $\sigma = E_1\cdot\varepsilon(t - t_1) = -\eta\cdot d\varepsilon/dt$, from which: $\varepsilon = \varepsilon(t_1)\cdot\exp(-(t - t_1)/\tau)$ with, again, $\tau = \eta/E_1$.

6.7. The strain after removal of the stress approaches tot 0, and there is also an elastic strain of 1 cm (retraction from 5 to 4 cm strain), A possible model is, therefore, a Kelvin-Voigt element (with E_1 and η parallel), in series with a spring E_2. From the immediate jump in the strain after stress release ($\sigma = 10^4$ N/10^{-4} m^2 = 10^8 Pa), it follows: $\varepsilon_2 = 1/20 = 0.05 = \sigma/E_2 = 10^8/E_2$, so $E_2 = 20\cdot10^8$ Pa = 2000 MPa.
Now the Kelvin-Voigt element: from $\Delta l = 4\cdot\exp(-2t)$ it follows $\tau = \frac{1}{2}$ hour = 1800 sec $= \eta/E_1$. The strain during the first 5400 sec can thus be represented by:
$\varepsilon = \varepsilon_2 + (\sigma/E_1)\cdot(1 - \exp(-t/\tau)) = 0{,}05 + (10^8/E_1)\cdot(1 - \exp(-3)) = 0.5$, from which (with $e^3 = 20$) follows: $E_1 = 475$ MPa. With $\tau = 1800$ sec this results in: $\eta = 1800\cdot 4.75\cdot10^8 = 855\cdot10^9$ Pa·s. The model is shown in the figure.

6.8. Now the strain, after stress release, approaches to 0.5 cm, which is a permanent strain $\varepsilon_3 = 0.5/20 = 0.025$ as a result of the dashpot in series in the model. The viscosity, η_2, of this dashpot is given by: $\varepsilon_3 = \sigma\cdot t/\eta_2$ or $0.025 = 10^8\cdot 5400/\eta_2$, so ($\eta_2 = 21.6\cdot10^{12}$ Pa·s.

The elastic deformation is now 0.5 cm or $\varepsilon_1 = 0.025$,, so the spring in series has a stiffness $\sigma/\varepsilon_1 = 10^8/0.025 = 40\cdot10^8$ Pa = 4000 MPa.

For the Kelvin-Voigt element remains:

$\varepsilon_2(5400 \text{ sec}) = (4 \text{ cm}) = 0.2 = 10^8/E_1\cdot(1 - \exp(-5400/1800)) = 0.95\cdot10^8/E_1$, so $E_1 = 475\cdot10^6 = 475$ MPa. Since $\tau = 1800$ sec, $\eta_1 = 1800\cdot 475\cdot10^6 = 855\cdot10^9$ Pa·s.

The model is, therefore, as shown in Figure A.16.

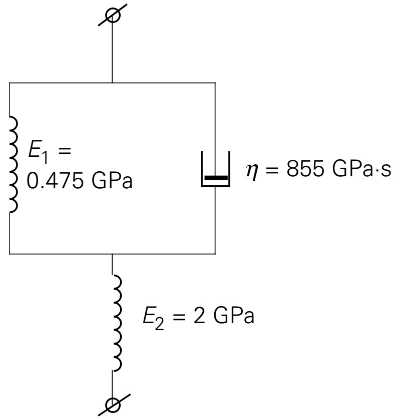


Figure A.15. Figure to the answer of problem 6.7.

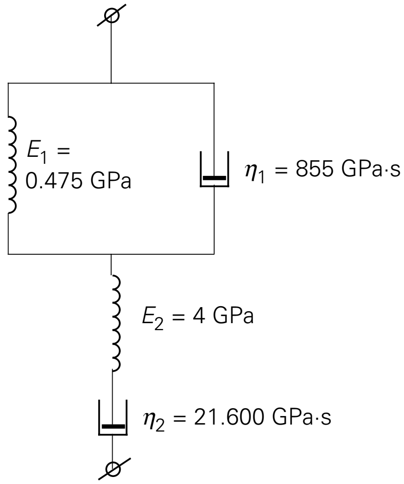


Figure A.16. Figure to the answer of problem 6.8.

6.9. Let the deformation of the spring E be ε_1 and of the dashpot: ε_2. Their sum, $\varepsilon = \varepsilon_1 + \varepsilon_2$ is equal to $v \cdot t$, in which v is the constant rate of strain, $d\varepsilon/dt$. The stress is given by $\sigma = E \cdot \varepsilon_1 = \eta \cdot (d\varepsilon_2/dt)$.
With $(d\varepsilon_2/dt) = v - (d\varepsilon_1/dt)$ we find: $v = (E/\eta) \cdot \varepsilon_1 + d\varepsilon_1/dt$, from which, after solving, it follows that: $\varepsilon_1 = v \cdot \tau \cdot (1 - \exp(-t/\tau))$ with $\tau = \eta/E$.
So thhe σ - ε diagram (see Figure A.17) looks as follows: $\sigma = E \cdot v \cdot \tau \cdot (1 - \exp(-t/\tau) = \eta \cdot v \cdot (1 - \exp(-t(\tau))$.

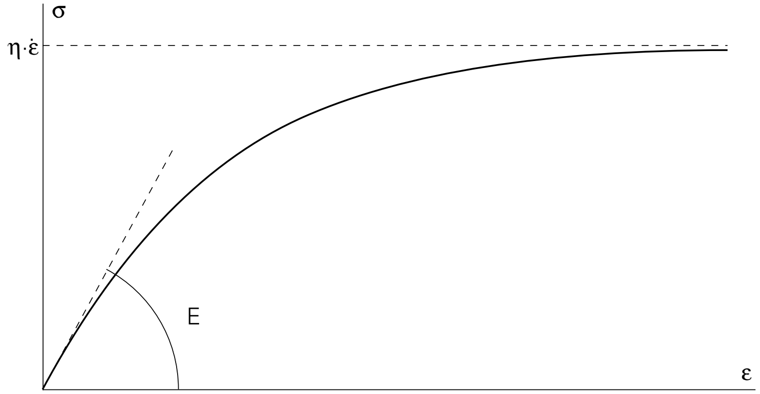
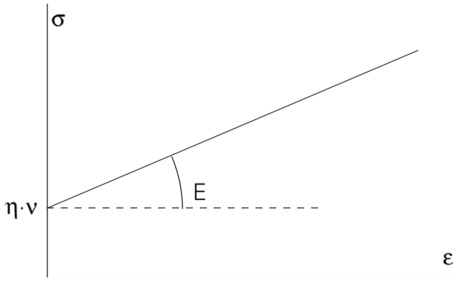


Figure A.17. Figure to the answer of problem 6.9.

6.10. Again: $\varepsilon = v \cdot t$. Now the stress on the spring is $\sigma_1 = E \cdot \varepsilon = E \cdot v \cdot t$, and on the dashpot: $\sigma_2 = \eta \cdot v$. The total stress is $\sigma = v \cdot (E \cdot t + \eta) = (\varepsilon/t) \cdot (E \cdot t + \eta) = \varepsilon \cdot (E + \eta/t) = \varepsilon \cdot E + \eta \cdot v$.



Figuur A.18. Figure to the answer of problem 6.10.

6.11. Apparently the stress relaxation proceeds in two phases, each with a stress decrease of 1 MPa at a strain $\varepsilon = 1$. It seems logical to think of a parallel arrangement of two Maxwell elements, both with a spring constant $E = 1$ MPa, but with relaxation times which differ by a factor 10,000 . Inspection of the stress values (with $\sigma = \sigma_o \cdot \exp(-t/\tau)$) easily results in: $\tau_1 = 1$ sec, $\tau_2 = 10{,}000$ sec. The viscosities are then: ($\eta = \tau \cdot E$): 10^6 and 10^{10} Pa·s.

6.12. *a.* E_1 is the storage modulus, and indicates how much reversible energy is stored in the material (purely elastic). E_2 is the loss modulus; it is a measure for the energy lost during deformation i.e. dissipated into heat; it thus signifies the contribution of the fluid nature of the material.

b. Vibration experiments, e.g. with a torsion pendulum, yield E_1 from the vibration time and E_2 from the damping of the vibration (see MT 6.2).

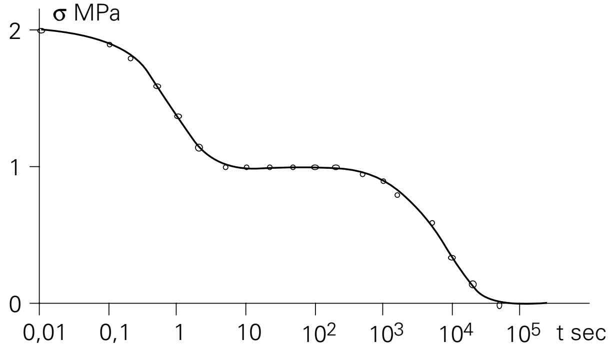


Figure A.19. Figure to the answer of problem 6.11.

c. The ratio of these two quantities, E_2/E_1, is tan δ, which is, therefore, a measure for the position of the material in the visco-elastic region ($\delta = 0$: purely elastic; $\delta = \frac{\pi}{2}$ (90°): purely viscous)

d. – heating under repeated stress cycles (e.g. with fatigue).

- damping of shock waves, e.g. with rubber-modified polymers,
- use of a polymer for damping of vibrations,
- heating of an automotive tyres,

– friction of a tyre on the road (see MT 7.3)

6.13. *a.* a. The curve *p* is typical for an amorphous, not cross-linked polymer; *q* for a cross-linked polymer,

b. For both curves the maximum lies at the glass-rubber transition temperature T_g,

c. For *p* the polymer gradually shifts into the liquid condition; δ increases up to $\frac{\pi}{2}$ and tan δ to infinity,

d. In a network (*q)* the loose chain ends (not held between two cross-links) do not contribute to the network elasticity, but they behave more or less as a fluid. Therefore, with increasing *T*, tan δ approaches to a finite value, dependent on the network structure.

7. Mechanical properties

7.1. The cross section of the bar is $10^{-2}\cdot 10^{-3} = 10^{-5}$ m^2. The stress is $\sigma = 600/10^{-5} = 60\cdot 10^6$ Pa = 60 MPa. The elongation is $\varepsilon = 2/100 = 0.02$. The modulus of elasticity is $E = \sigma/\varepsilon = 60/0.02 = 3000$ MPa. = 3 GPa.

7.2. A value for *E* of about 3 GPa is normal for an amorphous polymer in the glassy state, unless below T_g a strong secondary transition occurs such as with PC, so that the E-modulus at ambient temperature is significantly lower.

7.3. With semi-crystalline polymers we should always carefully distinguish between the behaviour below T_g and above T_g. Below T_g (such as with PEEK) the crystalline fraction, which is somewhat stiffer than the amorphous glass, dominates, so that E is somewhat higher. Above T_g, such as with PE and PP, the amorphous fraction, which is in the rubbery condition, is responsible for a significantly lower *E*.

7.4. – By chain orientation, such as in fibres,

– by “reinforcing” fillers, such as hard particles or short fibres.

7.5. Tighten both bars at equal length in a clamping-screw, bring them in a bending vibration and listen to the pitch. The highest tone is given by the stiffest bar, which is the bar made of pure PP. Musical people may be able to estimate the interval between the two tones; if this is, e.g. a whole-tone distance (12% in the frequency), we know that the ratio of their E-moduli is about $(1/1.12^2) = 0.8$. With the Kerner formula (Chapter 9) we can now estimate the rubber content.

7.6. Fibres are, as a result of the spinning process, molecularly oriented, and they have, therefore, a 2 to 3 times higher stiffness than the non-oriented polymer (e.g. polyamide and polyester textile fibres). With the highest attainable orientation, such as in aromatic polyamides (Twaron and Kevlar), and in the PE-fibre (Dyneema) the stiffness can be a hundred times higher than the one in the unoriented condition!

7.7. The chain stiffness influences the height of the glass-rubber transition temperature (and of the melting point), but not the stiffness of the polymer below T_g (in the glassy state). Extremely stiff chains show the effect of the formation of LCP's (liquid-crystalline polymers), by which very high stiffness is reached, but only in the direction of the orientation.

7.8. In principle a shifting rule could be applied, but the volume retardation (physical ageing) is responsible for a gradual increase of the resistance against creep, so that the rate of creep gradually decreases. Creep curves at e.g. 20 °C thus proceed considerably less steep, and the real creep is therefore (fortunately!) much less than would follow from the T-log t shift (see MT 7.2.4).

7.9. *See Figures A.20, A.21 and A.22.*

a. could possibly apply to a semi-crystalline polymer with a T_g not too far above ambient temperature, so that E (below T_g) is still high; at longer times of loading the polymer A "creeps gradually towards T_g" (example: PETP).

b. could apply to an amorphous glassy polymer; E has its normal high value (about 3 GPa), while T_g is high enough to be not approached at longer times of loading (example: PMMA).

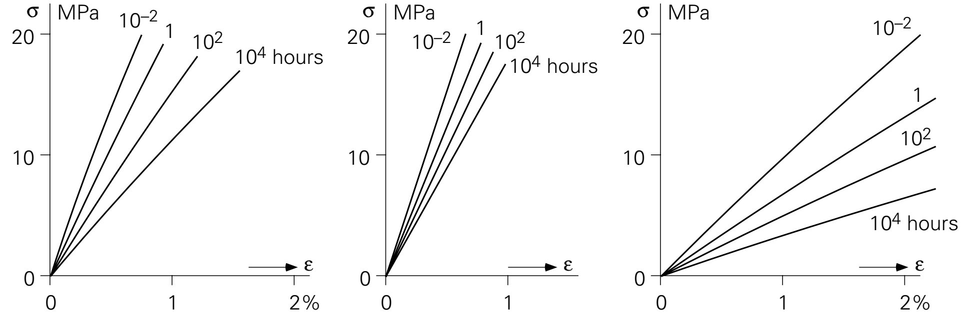


Figure A.20 — 22. Figures to the answer of problem 7.9.

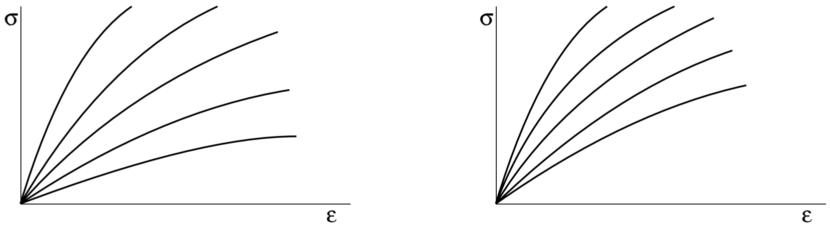
c. The low E-modulus could indicate a semi-crystalline polymer above T_g such as PP; the strong creep of a crystalline - rubber two-phase system is also in accordance with this assumption.

7.10. The Kohlrausch formula is well suitable to represent the creep at small stresses and strains. D_0 is then the compliance at t = 0, and is a measure of the immediate elastic deformation. The formula, however, fails when the creep behaviour is non-linear; this is, in general, the case with stresses occurring in practice.

7.11. *a.* After cooling to below T_g the volume of a glassy polymer continuously decreases gradually (see MT 3.3.): "volume-retardation".

b. The resistance against creep increases strongly by volume retardation.

c. See Figure A.23.



without *with physical ageing*

Figure A.23. Figure to the answer of 7.11 c.

7.12. Noryl (homogeneous blend of PPE and PS) is an amorphous polymer in the glassy state. It shows relatively little creep; the isochrones lie close to each other. With PBTP the distance between isochrones is much greater: there is more creep. This is related to the semi-crystalline structure of PBTP (contrary to PPE/PS). Though the glass-rubber transition temperature of PBTP, T_g, is about 65 °C, this transition is already apparent at lower temperatures and longer loading times. The polymer belongs, therefore, to the category described in MT 4.5, Figure 4.20.

7.13. *a.* Can be read off directly from the 10^2 hour isochrone at 8 MPa: $\varepsilon = 1.33$ %.

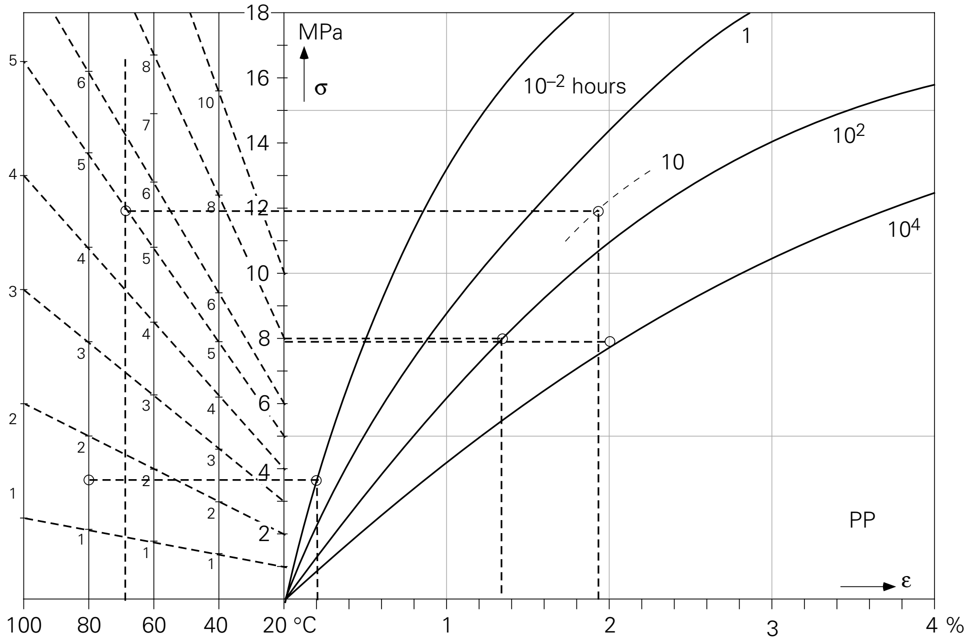


Figure A.24. Figure to the answer of problem 7.13a.

b. At 70 °C we choose the axis half-way between 60 °C en 80 °C; for 10 hours an isochrone half-way between 1 and 100 hours, and we find at 5 MPa: $\varepsilon = 1.94\%$.

c. For the short-time modulus we take the slope of the 10^{-2} hour isochrone, and we read off at 20°, e.g. at 0.2% : 3.4 MPa. It follows then that $E = 3.4 / 0.002 = 1700$ MPa.

d. With the same isochrone we find at 80^{o} and 0.2%: 1.3 MPa, so $E = 1.3/0.002 = 650$ MPa.

e. 1 year = 8766 hours, so close to the 10^4 hours isochrone. With $\varepsilon = 2\%$ we find at 20 °C about 8 MPa as an allowable stress.

f. At 100 °C and 1000 hours (half-way between the 10^2 and 10^4 isochrones), we find for 3% about 3.7 MPa.

7.14. Plotting times to failure (log *t*, horizontal) versus applied stress (log σ, vertical, different scale), results in the following figure:

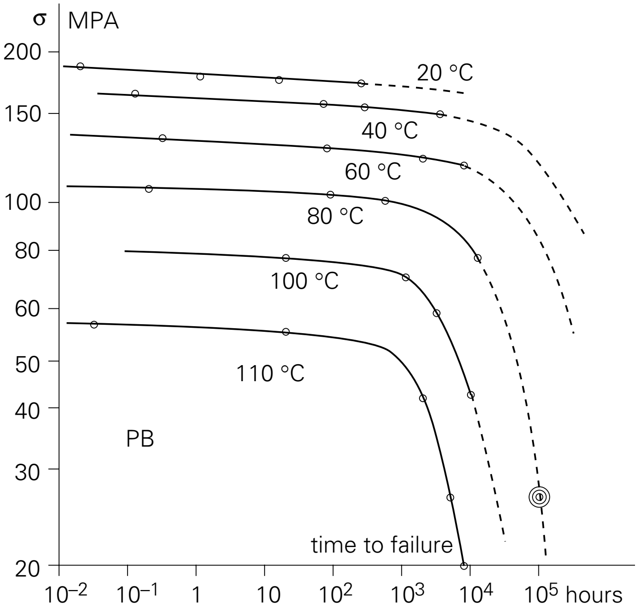


Figure A.25. Figure to the answer of problem 7.14.

From this figure, safe wall stresses at various temperatures and loading times can be determined by extrapolation. We extrapolate the curves found at higher *T* to lower *T*'s. Here a ten years life (87,660 hours) at 80 °C is required. Extrapolation of the curve for 80 °C results in an estimated stress to break of 28 MPa. To remain at the safe side, we stay somewhat below this value, so that 20 MPa looks a reasonably safe wall stress for this purpose.

7.15. *a*. First damage can occur by "crazes" (see MT 7.4.2)
b. To avoid "crazes" completely, we have to stay below a "critical strain", which, for each polymer is about a material constant. To remain within this limit the use of creep isochrones is required..

7.16. First: A well defined notch forces the sample to break at that place because of the stress concentration, and not at an accidental scratch or contamination. The results are, therefore, better reproducible.
Secondly: At the location of the notch the rate of deformation is considerably higher than in the remainder of the sample. The higher rate of strain has a similar effect as a temperature decrease, so that one measures, as it were, at a lower T, with a much greater chance of brittle fracture (which is important for practical use) (see MT 7.4.3).

7.17. *a*. Improvement of impact strength can be reached by adding a dispersed rubbery phase.
b. The rubbery phase introduces a glass-rubber transition at the T_g of the rubber, and, therefore, a damping peak which is able to absorb shock energy (analogous to some secondary transitions in the glassy region, such as with PC). Moreover we can think of the ‘neutralisation’ of a just initiated crack in a dispersed rubber particle.
c. At the T_g of the added rubber the E-modulus of the blend necessarily decreases; in the temperature region of use we, therefore, lose in stiffness.
d. Examples: TPS (toughened polystyrene) or HIPS (high-impact PS) or SB (styrene-butadiene); also PP copolymer, a PP with "tails" of ethylene-propylene copolymer, which form a rubber phase, PVC with CPE (chlorinated PE), etc. etc.

7.18. The impact strength of a polymer is strongly dependent on the molar mass, in particular on $\bar{M}_n$ (number average, number of chain ends)

7.19. *a*. In a Shore-D hardness test the penetration of the pin is measured during loading; the load is thus prescribed as well as the resulting deformation (see MT 7.5.1).
b. The time scales of both measurements may differ considerably; moreover, with a hardness test we may enter into the non-linear region.
c. A hardness test is, with a simple apparatus, much easier than a measurement of the E-modulus, which requires the measurement of a stress-strain diagram and the determination of its initial slope.

7.20. The higher the temperature above T_g, the more we are removed from the damping peak, so the lower is tan δ.

7.21. With increasing T, tan δ approaches to a limiting value, which is governed by the network perfection, in particular by the number and length of loose chain ends, which as it were represent a fluid component.

8. Further properties

8.1. With an amorphous thermoplastic the brittleness temperature is about T_g, unless a secondary transition temperature T_{sec} occurs in the glassy region; in that case the brittleness temperature may be in the neighbourhood of T_{sec}.

- with a semi-crystalline polymer the brittleness temperature is about T_g.
- with a rubber-modified thermoplast the brittleness temperature is about the T_g of the dispersed rubber.

8.2. With an amorphous thermoplast the polymer softens over a rather short temperature interval from the glassy to the rubbery state. With a semi-crystalline polymer a certain amount of softening takes place at T_g; with further T- increase the stiffness drops very gradually up to the melting point T_m.

8.3.	PBTP	PTFE	PP	PMMA	PA 6.6	POM	HDPE
ISO-A from table	60	55	60	95	90	115	45
ISO-A estimated from $E(T)$	40	25	50	80	90	115	65
Vicat B from table	180	110	90	100	230	165	70
Vicat B estimated from $E(T)$	150	130	140	90	240	180	110

The agreement is reasonable, though not perfect. Differences can be accounted to:

- small differences between the samples taken,
- differences in the time scales of measurements,
- non-linear behaviour (in particular with the Vicat test).

8.4. *a*. The contradiction is a result of the slope of the log E - T curves (see MT 8.1.2).

b. The ISO-A test is carried out at a higher E-modulus level than the Vicat test, thus giving more information for applications where a higher E is required, i.e. in loaded condition.

8.5. The blending of short glass fibres results in an increase of the E-modulus to e.g. its threefold over the whole temperature region. If the slope of the log E - T curve is small. such as with semi-crystalline polymers between T_g and T_m, a vertical shift causes a considerable horizontal shift (see MT 8.1.2.), so a strong increase of the softening points, which are of importance in applications at higher temperatures.

8.6. The high coefficient of expansion can cause problems with shape stability and dimension tolerances in precision products. Moreover the high expansion causes more shrinkage upon cooling after a shaping process (see e.g. MT 10.3.2).

8.7. Advantages:

- various applications in which, e.g. a handle remains cool ; also in foams for thermal insulation it is important that the cell walls do not conduct too much heat.

Disadvantages:

- With repeated changes of load the dissipated heat cannot easily flow away, so that the temperature of the object increases and it loses its good mechanical properties.
- In a processing operation the heating-up and, thereafter, the cooling-down, are troublesome operations because of the low thermal conduction. In heating-up use can be made of friction or dielectric effects etc. (see MT 10.1.1), but with cooling the low heat conduction mainly governs the cycle time.

8.8. *a.* (see MT 8.1.4): $\lambda = \lambda_p + \lambda_g + \lambda_r + \lambda_k$ (polymer conduction + gas conduction + radiation + gas convection).

b. Larger cells : more convection; larger λ_k , so λ increases.

c. Lower density: lower λ_p, but higher λ_r (radiation passes through cell walls), therefore a minimum in λ.

d. λ_g depends on the type of gas (heavier gas: lower λ_g).

e. The lowest possible minimum is λ_g, the coefficient of conduction of the gas in rest.

8.9. Firstly: Though a high softening temperature is attractive, we should realise that the polymer has to undergo processing operations, which are carried out, for an amorphous polymer, well above T_g , and for a crystalline polymer, above T_m. At these temperatures the polymer should be sufficiently chemically stable (for i.a. that reason PPE is being blended with PS).

Secondly: For long-term applications not only the softening point is of importance, but also the degradation behaviour of the polymer; it may quite well happen that the polymer suffers unallowable degradation considerably below its softening T (see MT 8.1.5)

8.10. *a.* The term “stress corrosion” signifies damage (crack formation) under simultaneous presence of a mechanical stress and a certain environment, which both in itself are not fatal.

b. The word “corrosion” suggests that a chemical reaction is involved, but in several types of stress corrosion no chemical degradation occurs, but it is caused by a lowering of the interfacial energy (such as with PE with a surface active agent). Another example of “physical” stress corrosion is the effect of e.g. tetrachloromethane on PC.

c. In those cases when chains are actually broken we have to do with real stress corrosion, such as the effect of ozone on a rubber vulcanisate.

d. see above.

8.11. – To avoid risks of electrostatic charging (sparks, explosions) anti-static additives are sometimes added to a polymer; also carbon black may be used (see MT 8.2.1).

- Polymers are sometimes used to shield electromagnetic fields; for this purpose they can be filled with metal fibres.
- In extreme cases conjugated dienes with an adequate doting can reach an electric conductance similar to that of metals.

8.12. The electrostatic charging is mainly controlled by the specific resistance of the material (sometimes also by the surface resistance). Decrease of the tendency to build up electrostatic charges can, therefore, be reached by lowering the specific resistance or the surface resistance, e.g. by adding carbon black or short metal fibres, or by using anti-static agents. The time scale is important because each application presents its own requirements as regards the dissipation of the charge, e.g. the formation of sparks or the attraction of dust (see MT 8.2.1).

8.13. Advantages:

- The low tan δ of PE at very high frequencies enabled the application of radar in the 1930's.

Disadvantages:

- PE cannot be heated in a high-frequency electric field for, e.g., welding films. Special "tricks" are then needed, such as coating the film with a thin layer of a polymer with a higher tan δ.

8.14. *a.* With precision optics dimensional tolerances are extremely narrow, so that even the smallest amounts of recovery are disastrous for the performance.

b. Advantages for spectacle glasses are: reduced weight and higher impact resistance. Disadvantages are the lower resistance against scratching (which can be improved by a coating), and, on the long term, the dimensional stability.

8.15. One of the main problems with a compact disc is the birefringence; the laser beam is split-up into two components, thus mutilating the signal. It is, therefore, important to reduce the birefringence; this can be done by minimising the chain orientations by choosing a PC with a low M. This is, moreover, beneficial for the ease of processing (very tiny details!), but is at the cost of the impact strength, which is, fortunately, for this type of application already high enough.

8.16. IIR (butyl rubber) is compared with other rubbers (SBR, NR) and then has a

20 to 30 lower permeability (inner tubes!). PE and PP are much more permeable than most of the other plastics. These phenomena can be attributed to the fact that the rate of diffusion in the rubbery phase (large free volume) is considerably higher than in the glassy-, and, in particular, in the crystalline phase. PE en PP contain, next to a crystalline phase, a continuous amorphous rubbery phase.

8.17. In the first place the rate of diffusion of LDPE is higher, as a consequence of the higher amorphous fraction. Secondly, for the same reason, LDPE has a higher solubility (the solubility in the crystalline phase is very low).

9. Polymeric compounds and composites

9.1. The molar masses are reflected in V_1 en V_2 (the molecular volumes). Increase of these values causes the first two (negative) terms to approach more to zero, so that a negative value of ΔG_m becomes less probable.

9.2. χ is related to the enthalpy of blending, and is positive when only dispersion forces are present between the chains, so that, in view of the small contribution of the entropy of blending (the first two terms), ΔG_m will be, in most cases, positive. With strong interactions χ becomes negative, and, at the same time, ΔG_m..

9.3. For $\varphi_1 = \varphi_2 = 0.5$ and $V_2 = V_1$ the formula reads::
$\Delta G_m/V = kT[-(\ln 2)/V_1 + \chi/4V_s]$. This is negative when $\chi/4V_s < (\ln 2)/V_1$ of: $\chi < 2.77(V_s/V_1)$.

9.4. At very small values of φ_1, ln φ_1 is so deeply negative that ΔG_m is negative, independent of the values of V_1, V_2, χ etc. The same holds for φ_2. The curve for ΔG_m as a function of f thus proceeds, at its extreme values, steeply downward, independent of how its further course looks like, e.g. as indicated in the figure.

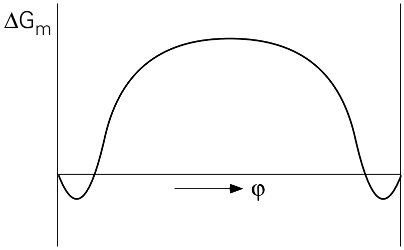


Figure A.26. Figure to the answer of problem 9.4.

9.5. When there is a UCST (upper critical solution temperature), then above that temperature the components are fully mixable. When cooling down to below this UCST a region of segregation can be reached, in particular when the volume fractions do not differ too much (see MT Figure 9.3, lower part "upside down")

9.6. Now about an LCST (lower critical solution temperature, see MT Figure 9.3). If we blend below this temperature, we can obtain a homogeneous mixture. Subsequent heating to above the LCST can result in segregation; the rapid cooling in an injection moulding machine does not allow to undo this.

9.7. For thermodynamic reasons mixability may be all right, but the last step in a mixing process, when the droplets are sufficiently small, is a diffusion process; this needs a considerable time, which is not always available in a blending process (in this way a "multiphase" blend could be formed, see MT Figure 9.4.d)

9.8. With very short "blocks", such as in the random-copolymer SBR, there is only a very small difference in entropy between the segregated and the homogeneous condition: no or hardly any change of entropy upon segregation. As the block length increases, this difference, however, increases, so that (G decreases (see MT 9.1.4). Segregation is, therefore, less complete in multi-block copolymers (such as polyethers- polyesters).

9.9. On the one hand in a flow field shear stresses τ are exerted on a droplet which cause a deformation into an ellipsoid; on the other hand the surface area of the droplet is increased by this deformation, so that the interfacial energy σ/R increases. When the size of the droplet decreases the first effect becomes smaller in comparison to the second one, which results in an equilibrium at which no droplets are broken-up (expressed in the capillary number $\mathrm{Ca} = \tau/(\sigma/R)$, (see MT 9.1.5).

9.10. The droplets may have been broken down to their minimum diameter, but in the flow field they meet, they collide, and they can coagulate into bigger ones. The blending process is, therefore, an ongoing competition between break-up of droplets and coagulation.

9.11. The first process is: the deformation of droplets into an ellipsoid, until the droplet breaks up. The second process is: A droplet is, at high speed, extended into a thread, which is subject to instabilities (according to Rayleigh and Tomatika), and which, therefore, breaks up into a row of droplets (see MT 9.1.5).

9.12. Series- and parallel arrangements provide a first approximation of the properties; the properties which follow from these arrangements, are widely different. Combinations of series- and parallel arrangements (Takayanagi) are able to provide good approximations, but they require a large number of parameters (see MT 9.1.6).

9.13. If we apply Kerner's formula to this PE, with $\varphi_{\mathrm{cr}} = 0.552$, for a continuous crystalline phase, in which an amorphous phase is dispersed, we find $\varphi = 0.448$, $A = 1.14$ (with $\nu = 0.33$), $E_o = 6000$ MPa, $E_1 = 1$ MPa (both estimated provisionally), so

$\alpha = 1/6000$.

$$E = 6000\cdot\frac{1 + 0.448\cdot 1.14\cdot(1/6000 - 1)/(1/6000 + 1.14)}{1 - 0.448\cdot(1/6000 - 1)/(1/6000 + 1.14)} = 2378 \text{ MPa}$$

With the inversed morphology, so crystalline dispersed in amorphous, we have: $\varphi = 0.552$, $E_o = 1$ MPa, $E_1 = 6000$ MPa, so $\alpha = 6000$, $A = 1.5$, and, according to Kerner:

$$E = 1\cdot\frac{1 + 0.552\cdot 1.5\cdot(6000 - 1)/(6000 + 1.5)}{1 - 0{,}552\cdot(6000 - 1)/(6000 + 1.5)} = 4.08 \text{ MPa}$$

With Nielsen's formula we find: $E = [0.552\cdot 6000^{0,2} + 0.448\cdot 1^{0,2}]^5 = 598.5$ MPa. Apparently the result of Nielsen's formula is closest to the observed E-modulus. With a few trials the values of $E_{cr} = 6400$ MPa and $E_{am} = 1.5$ MPa render the best agreement, viz. $E = 667$ MPa, compared to the observed value of 660 MPa. Conclusion: In PE the crystalline phase and the amorphous phase are both continuous and "interwoven".

9.14. *a*. 150S + 2000B + 150S = (with S = 104, B = 54) = 15,600 + 208,000 + 15,600 = 139,200 g/mole; the weight fraction styrene w(PS) = 31,200/139,200 = 22,4%.

b. The mass of a PS end chain is $15{,}600/6.10^{23}$ g = $2.60\cdot 10^{-20}$ g. The volume of a PS domain = $(\pi/6)\cdot 25^3\cdot 10^{-21}$ cm^3 = $8.18\cdot 10^{-18}$ cm^3, its mass $V\cdot 1.05$ = $8.59\cdot 10^{-18}$ g. Divide: the number of PS chains in a domain is 330

c. Main cause: T_g is lower for PS domains because of its low M, compared to "normal" PS; the difference may be as high as 10 °C. (MT 3.4.3). Therefore at T_g-10 °C softening of the PS domains can already occur.

d. First we calculate the volume fraction φ of PS: 1 gramme SBS contains 0.224 g PS, so 0.224/1.05 = 0.213 cm^3 PS, and 0.776 g BR or 0.776/0.91 = 0.853 cm^3 BR. Total volume is 1.066 cm^3, of which 0.213 cm^3 PS, so $\varphi = 0.213/1.066 = 0.20$. Substituting this, with $\alpha = 1000$ and $A = 1.5$ (rubbermatrix), into the Kerner equation, results in: $E/E_o = 1.62$ so $E = 4.9$ MPa.

The PS domains not only act as cross-links, but they also increase the stiffness.

9.15. When a foam contains closed cells, we can apply Kerner's formula with $\alpha = 0$, so: $E/E_o = (1 - \varphi)/(1 + \varphi/A)$.

With $\varphi = 0.5$, $E_o = 3200$ MPa and $A = 1.14$ (for $\nu = 0.33$) we find: $E = 1112$ MPa.

An open cell foam is a co-continuous structure, sot that Nielsen's formula can be applied: $E^n = \varphi_1 E_1^n + \varphi_2 E_2^n$ with $n = 0.2$, $\varphi_1 = 0.5$, $E_1 = 3200$ and $E_2 = 0$ (gas!); this results in: $E = (\frac{1}{2})^5\cdot 3200 = 100$ MPa.

The conclusion is that the first foam has closed cells, the third one is completely open-celled and the second one contains partly open, partly closed cells.

9.16. For a "heavy" foam the gas fraction φ is small. The Kerner formula for a foam

with closed cells: $E/E_o = (1 - \varphi)/(1 + \varphi/A)$ can then be approximated by: $E/E_o = 1 - \varphi - \varphi/A = 1 - (1 + 1/A)\cdot\varphi$. For rubbers with $A = 1.5$ this becomes: $E/E_o = 1 - 1.7\cdot\varphi$, for glassy polymers with $A = 1.14$: $E/E_o = 1 - 1.9\cdot\varphi$. When we use the approximation to $1 - 2\varphi$ or $(1 - \varphi)^2$ (always for small φ), and we realise that $1 - \varphi$ is proportional to the foam density, then from this approximation it indeed follows, in particular for hard thermoplastics, that: E (:) d^2
The approximation seems somewhat rough, but it appears to fit reasonably.

9.17. With the introduction of particles in a polymer the stiffness increases, but the tensile strength and the impact strength are hardly increased. It is, therefore, better, to use the term: ‘stiffening additives’.

9.18. Carbon black increases the tensile strength of an SBR vulcanisate to its 10 to 20-fold (which would, otherwise, be very low), as well as its abrasion resistance. Natural rubber can, because of its stereospecific (cis) chain structure crystallise under strain, and, therefore, reach higher values of its tensile strength; for a good abrasion resistance carbon black is also of importance with NR.

9.19. A continuous phase forms a "skeleton" in the blend. This is important, e.g. in the following cases:

- a second phase with a considerably higher softening temperature; when the other phase softens, the skeleton retains its stiffness.
- an electrically conducting polymer as a second phase provides the wanted conduction.
- an impermeable polymer as the second phase renders the blend impermeable only if it forms a continuous network.

9.20. *See Figure A.27.*

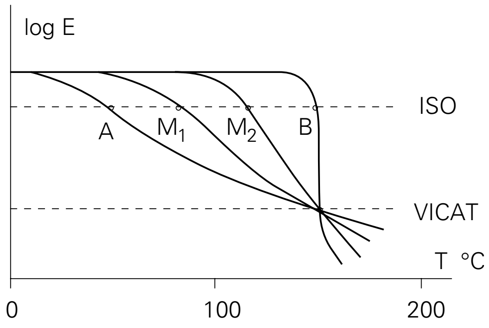


Figure A.27. Figure to the answer of problem 9.20.

Apparently all four curves intersect at the same point, namely at the temperature at which A and B have the same E-modulus. Each blend has the same modulus at this temperature. This situation may occur when B is a glassy amorphous polymer and A is semi-crystalline. The behaviour of Xenoy (PC + PBTP) resembles this picture.

9.21. *See Figure A.28.*
The four curves have about the same shape; they are shifted along the *T*-axis. C and D are typically amorphous polymers. They are wholly miscible. The pattern resembles the one of Noryl (PPE + PS).

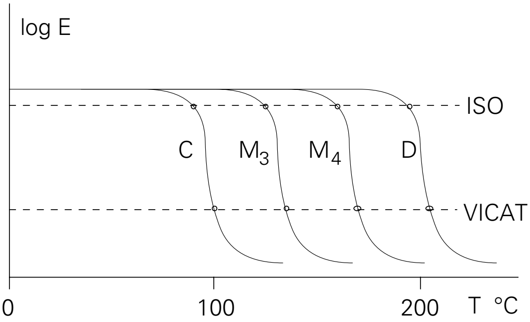


Figure A.28. Figure to the answer of problem 9.21.

9.22. Apparently two opposing effects play a part: On the one hand the glass fibres take over a part of the stress, thus partially releasing the stress on the polymer. On the other hand, fibres cause, in particular at their ends, stress concentrations, which can initiate crack formation.

9.23. E_o = 3000 MPa, E_1 = 2 MPa, so $\alpha = 1/1500$, so α can safely be assumed as zero in Kerner's formula. From $\nu = 0.33$ it follows: A = 1,14. The value aimed at is E = 2400 MPa. From Kerner it follows: $0.8 = (1 - \varphi)/(1 + \varphi/1.14)$, so $\varphi = 0.1175$. easy rule of thumb: the percentage of modulus reduction is about twice the volume percentage of rubber, or also gas bubbles).
The mass fraction is: $\psi = \varphi{\cdot}\rho_r/\rho_{pr}$ in which ρ_{pr} is the density of the polymer - rubber blend: $\psi = \varphi{\cdot}\rho_r/[(1 - \varphi){\cdot}\rho_p + \varphi{\cdot}\rho_r] = 0.1175{\cdot}0.9/(0.8825{\cdot}1.4 + 0.1175{\cdot}0.9) = 0.106/1.34 = 0.079 = 7.9$ % w.

9.24. In the blend of the previous question we blend glass fibres. Now E_o = 2400 MPa and E_1= 75,000 MPa, so $\alpha = 31.25$. E should be increased up to 3000 MPa so $E/E_o = 1.25$. When we substitute this into the Kerner equation, again with A = 1.14 (not wholly correct since n has become somewhat higher because of the blending with rubber), Kerner's formula then becomes:
$1.25 = [1 + \varphi{\cdot}(1.14{\cdot}30.25/32.29)]/[1 - \varphi{\cdot}(30.25/32.39)]$, from which it follows:: φ = 0.112 of 11.2 %. The mass fraction is now, calculated on the polymer-rubber blend (ρ_{pr} = 1.34): $\psi = 0.112{\cdot}2.4/(0.888{\cdot}1.34 + 0.112{\cdot}2.4) = 0.184 = 18.4$ %w.

9.25. In a composite one aims at the highest possible stiffness E at the lowest possible ρ, so at a high as possible value of E/ρ, and this is the square of the sound velocity in the material.

9.26. The limit is reached when the glass fibres are so long that they can be considered as a continuous phase. We have then a parallel arrangement of polymer and glass, with $\varphi_1 = 0.75$, $\varphi_2 = 0.25$, $E_1 = 3$ and $E_2 = 75$ GPa. The E-modulus of the composite then follows from: $E = 0.75 \cdot 3 + 0.25 \cdot 75 = 21$ GPa.

9.27. The Einstein formula $E = E_o\,(1 + 2.5\varphi)$ is valid if α is rather high and α is rather small, and it gives, for the transverse direction: $E = 3\,(1 + 2.5 \cdot 0.25) = 4.9$ GPa. (The calculation with Kerner is better, but we now aim at a simple first approximation).

9.28. In an isotropic composite (chaotic distribution of fibre direction) E is given by: $E = 0.2 \cdot \mathrm{E}_{par} + 0.8 \cdot E_{transv}$. The first term follows from the answer to Question 19, the second one from 20, and the result is: $E = 0.2 \cdot 21 + 0.8 \cdot 4.9 = 8.1$ GPa. This value, therefore, approximates the highest attainable value with 25 vol% of glass fibres.

9.29.	glass fibres	rubber particles
a. T_g	no change	no change (there is an extra transition, namely of the rubber phase)
b. Vicat	higher	lower (shift effect *E*(*T*) curves, see MT 8.1.2)
c. T_m	no change	no change
d. ISO-HDT	higher (see *b.*)	lower
e. E-modulus	higher due to hard inclusions	lower, due to soft inclusions
f. tensile strength	slightly higher	lower
g. heat conduction	higher due to glass fibres	about the same
h. impact strength	sometimes better, sometimes worse	considerably higher (see MT 9.3)

10. Processing techniques

10.1. *a.* Heating from the outside (metal or infrared); controlled by heat conduction λ;

b. Friction (between granules, controlled by the friction coefficient μ), or in the liquid, (controlled by the viscosity η);

c. High-frequency dielectric heating, controlled by the dielectric loss factor tan δ;

d. Ultrasonic sound, controlled by the mechanical loss factor tan δ.

10.2. Casting is, of course, possible when the material is fluid enough. This is the case with some thermosets (casting resins), which, together with a second component, can be cast into a mould and then cured at a higher temperature.
With thermoplastics casting is, in general, not possible because of the high melt viscosity, except when polymerisation has still to take place; the monomer or pre-polymer is polymerised in the mould. This is, e.g. possible with PMMA and PA-6 (from methyl-methacrylate and caprolactam, respectively).

10.3. With semi-crystalline polymers the rubbery region is partly or wholly masked by the crystalline phase. Only very high-molecular grades types have part of the rubbery region left above their T_m. Processing techniques in which the rubber-elastic behaviour is essential, such as calendering and vacuum forming, are therefore less suitable for crystalline polymers, unless they have a very high molar mass.

10.4. When moulding thermoplastics the mould has to be heated, and, after shaping. cooled down to enable the taking-out of the product. This requires repeated changes in temperature of large blocks of metal. With thermosets and rubbers the temperature can remain high after shaping to enable curing or vulcanisation.

10.5. *a*. Two methods may be applied:

- injection moulding,
- forming from an extruded sheet.

  Both can lead to economic production. With the popular brown or white coffee-cup the second method (two steps) has, apparently, won the competition. Transparent PS cups are mostly injection-moulded.

b. The bottom of the injection-moulded cup shows the point of injection. Moreover, after sheet forming the wall thickness is less uniform than after injection-moulding.

c. An injection-moulded cup will gradually soften upon heating, whereas a vacuum-formed one first contracts into a flat sheet.

d. The choice between the possible processing methods is i.a. governed by the economy of production; this is strongly related to the production size (see MT 10.1.2).

10.6. *a*. At a certain injection pressure p, a minimum temperature T is needed to reduce the viscosity sufficiently to enable complete mould filling. A lower T requires a higher pressure.

b. The mould B requires a higher pressure to be filled; so it has a higher flow resistance (narrower) or a longer flow path (l/d).

c. In B the melt flows less easily than in A (higher viscosity); at first sight we could suppose that B has a lower melt flow index (m.f.i.)

d. If, however, the m.f.i. of B appears to be higher than that of A, then A has a much broader molar mass distribution; it is stronger non-Newtonian, so that it flows better at the high shear rates in the machine, despite of its lower m.f.i.

e. At further increase of the pressure the mould halves may be pushed apart, because the clamping force is insufficient ("flash").

f. A too high temperature may lead to degradation of the polymer.

g. A too low T involves the risk of incomplete or non-homogeneous melting of the material.

10.7. *a.* When the pressure in the mould is 800 bar (1 bar = 10^5 N/m^2), the material exerts on the area of 100 cm^2 a force of $800 \times 10^5 \times 10^{-2}$ N = 800 kN ("80 tonnes"). This is thus the minimum required clamping force.

b. In the mould a volume is present of $10 \times 10 \times 0.3 = 30$ cm^3. At atmospheric pressure and 220 °C this would mean 30/1.34 = 22.4 grammes. At 800 bar the specific volume is, however, a fraction $800 \times 7.5 \times 10^{-5} = 0.06$ or 6% smaller, the mass is 6% greater, or $22.4 \times 1.06 = 23.7$ g. For the end product, at 1 bar and 20 °C this would mean a volume of $23.7 \times 1.05 = 24.9$ cm^3 or 24.9 / 30 = 0.83 times the volume of the mould. This means a volume shrinkage of 17% or a linear shrinkage of about 5%. The dimensions would be about 9.5 cm × 9.5 cm × 2.85 mm.

d. After filling of the mould extra space becomes available by cooling and solidification along the walls; maintaining the pressure until the polymer at the injection gate is also solidified will then enable several percents extra supply (after-pressure).

10.8. PE, PP and PA are semi-crystalline polymers; melting and solidification go accompanied by a (though gradual) volume jump. PS, PVC and PC are amorphous thermoplastics; upon solidification they show no volume jump, but only a bend in the V-T relation.

10.9. The outer side cools and solidifies first; the inner part remains fluid the longest; its shrinkage in the final stage of solidification is constrained. Its density will, therefore, be lower than at the outer side and tensile stresses are being built up, even with the risk of void formation.

10.10. Powder (blend of resin and curing agent) is deposited on the metal via a fluid bed or electrostatic. Upon heating it flows and, at the same time, it is cured. The course of the viscosity in an analogous situation is given in MT Figure 10.8. Now, however, too slow curing results in dripping of the fluid, while a too rapid cure stagnates the flow so that the surface is not smooth.

10.11. Between the rolls of a calendar enormously high pressures are built up, needed to transport and shape the material at high speed. These pressures cause bending of the rolls, even though they are very heavily constructed. The result is that the sheet is too thick in the middle. By crossing the axles of the rolls this can be largely compensated (see MT 10.4.1).

10.12. With calendering and also with vacuum forming the polymer must be in the rubbery condition; in the first case the sheet must be taken off from the last roll under a certain stress, which it can withstand in the rubbery phase only. With vacuum forming the heated sheet is placed on the mould; this is only possible when it possesses enough coherence and handability. The word 'molten' is therefore not relevant in these cases.
In other processes such as blow-moulding and film extrusion some rubber-elastic response also plays a part, though considerably less than in the examples mentioned before.

10.13. First: a broad molar mass distribution helps to lower the apparent viscosity at high shear stresses and shear rates, so that thinner films can be produced at the same pressure.
Secondly: a broader MMD leads to a higher value of $\overline{M}_z$, the average which is mainly responsible for the elastic behaviour of the melt, and thus for the recoil after deformation and solidification. These frozen-in rubber-elastic deformations cause the behaviour of shrink-films.

10.14. In rotation moulding the shear stresses and shear rates are extremely low; the polymer particles flow together into a homogeneous wall under the influence of gravity and surface stresses only. The relevant viscosity is, therefore, the "Newtonian" viscosity, without the complication of 'shear-thinning'.
So the width of the MMD is not of primary importance: only the weight average, $\overline{M}_w$ counts. A consequence is, that for a given m.f.i. the distribution should be narrow (see MT 5.4).
At the same time, with a narrow distribution $\overline{M}_n$ is higher since it closer to $\overline{M}_w$, This is important for the resistance against stress corrosion, since this is related to $\overline{M}_n$ (good for oil tanks).

10.15. Melt fracture results from a too large rubber-elastic deformation. This is governed by the polymer behaviour and by the rate of deformation. The strain rate must be lowered, which may be accomplished by a lower, and therefore unattractive, rate of production. The time scale of the elastic deformation can also be increased in another way, namely by making the conical channel to the die more pointed; the same strain is then reached after a longer time. This goes at the cost of extra pressure and power, since the resistance of the channel is increased.

10.16. When a pipe is extruded, the melt has to flow round the 'spider' at which the

torpedo is suspended, and, thereafter, flow together perfectly. The risk is an imperfect welding, causing weaker spots at the weld lines or ‘spider lines’.
Also with injection moulding weld lines occur frequently. The best known example is the eye for the handle of a pail, which is the spot at which the stresses are highest during use!

10.17. Adiabatic: no exchange of heat with the environment. For an extruder this means that no heat is supplied from the outside, but the energy for melting is wholly supplied by the internal friction. This is ideal for homogeneous heating of the material, without the trouble of low heat conduction. This can be realised with larger diameters. In most cases the heating-up is a combination of wall heating and internal friction.

10.18. Along the screw of an extruder both transport flow and transverse flow occur. The latter provides a circulation flow, which promotes mixing and homogeneity.

10.19. *a*. Q is the throughput in volume per unit time.
p is the pressure in front of the die,
N is the rotational speed of the screw.
η is the viscosity of the melt,
a is a geometrical constant, related to the screw geometry.
b ditto,
c is a geometrical constant related to the die dimensions.

b. The maximum throughput is 80 dm^3/hour; this is reached when there is no die at the end of the extruder (drag flow only). The maximum pressure (for a given viscosity of the polymer) is 400 bar (extrapolated); this is reached when the die is closed.

c. When the rotation rate is halved, the screw characteristic shifts down in a parallel way, and it then intersects the vertical axis at 40 dm^3/hour. Both the throughput and the pressure are then halved.

d. When the die resistance is doubled, the slope of the line through the origin is halved. From the graph it can then be deduced: the rate of throughput, Q is lowered from 80 to 48 dm^3/hour, the pressure p increases from 100 to 160 bar.

e. When the viscosity becomes three times higher, both slopes are three times smaller; the rate of throughput, Q, remains 60 dm^3/hour (this also follows from $Q = N \times a \times c/(b + c)$, in which η and p do not appear), but the pressure p becomes 3 times higher, so 300 bar.

f. As a result of the non-Newtonian behaviour both expressions for the pressure flows ($b \times p/\eta$ and $c \times p/\eta$) are no longer valid. The curve for the die is now curled upward since the apparent viscosity decreases with increasing shear stress. Also the shape of the screw characteristic changes.

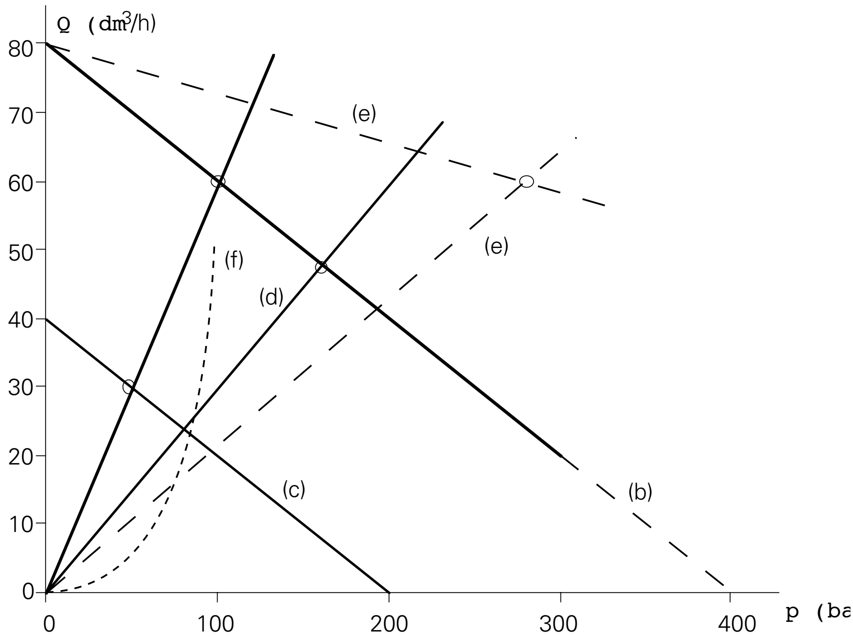


Figure A.29. Figure to the answer of problem 10.19 f.

10.20. *a.* Internal stresses are physically present stresses; frozen-in stresses are frozen-in chain orientations. The former result from uneven cooling from the melt: solidification first takes place at the cooled outer wall, while the inner parts solidify much more slowly, thus creating internal tensile stresses. The stress is, averaged over the cross-section, zero, but there is a stress distribution, composed of compression- and tensile stresses.

Frozen-in stresses originate from the rubber-elastic behaviour of the melt: the rubber- elastic deformations (chain orientations) are frozen-in upon cooling and remain present as 'latent' stresses.

b. Internal stresses (cooling- or shrinkage stresses) become apparent when from a ring, cut from a pipe, a small segment is removed; the ring will tend to close because the tensile stresses are mainly at the inside. Frozen-in stresses can be detected by heating a piece of a pipe to above T_g or T_m; the rubber-elastic stresses then get their chance to deform the sample to shorter and thicker dimensions.

c. Shrinkage stresses contribute to the total stress on a volume element in a pressure pipe. In the pipe a circumferential stress is present, on which, at the inner side, the shrinkage stress is superimposed. This may limit the life-time of the pipe.

Frozen-in orientations are present in the length direction of the pipe and may cause anisotropy: in the transverse- (circumferential-) direction the material is weaker, and this direction is just important for a pressure pipe! Moreover, at higher temperatures, the pipe may deform.

d. With thick-walled pipes cooling proceeds more slowly so that the shrinkage differences and the internal stresses become greater. Thin-walled pipes are extruded at a higher rate; the deformation of the melt takes place at a shorter time-scale, resulting in a higher rubber-elastic deformation. Moreover, the chain orientation is more readily frozen-in because of the quicker cooling.

10.21. *a*. PETP crystallises only slowly, and it stays amorphous in a normal injection-moulding process, after rapid cooling of the melt.

b. PETP has a T_g of about 70 °C and a T_m of 260 °C. If the pre-form would be semi-crystalline, then it could only be blown-up at a temperature above T_m. At such a T the viscosity is so low (condensation polymer, so not a very high M!), that blowing is not possible. Amorphous PETP can, at some distance above its T_g, easily be deformed in the rubbery condition.

c. During the blowing process the bottle is simultaneously stretched in the length direction so that a bi-axial orientation is reached, which is useful for the properties.

d. An amorphous bottle would soften completely already above 70 °C, so it would be hardly usable.

e. Chain orientation, also bi-axial, promotes rapid formation of nuclei, which is necessary to allow the polymer to crystallise sufficiently at a rather short time scale.

f. Because of the very large number of nuclei formed upon chain orientation, the crystallites remain small enough to avoid appreciable light scattering.

g. During spinning of polyester fibres such a high uni-axial orientation is brought away that rapid crystallisation occurs. This is, of course, essential for a good fibre.

10.22. *a*. Higher m.f.i.: lower M, so, in general, less elastic behaviour of the melt and a lower die-swell.

b. Larger ratio of m.f.i. at 10 and at 2.16 kg indicates a more strongly pronounced non-Newtonian behaviour, so a broader MMD with relatively more long chains (higher $\overline{M}_Z$), resulting in stronger elastic response of the melt and a higher die-swell.

c. At a higher rate of throughput the rate of deformation of the melt is higher, resulting in more elastic response and a higher die-swell.

d. At a higher temperature the relaxation times are shorter, so that there is less chance of chain orientation when the melt leaves the die.

e. Most of the rubber-elastic strain is brought about in the conical channel leading to the die (elongational flow).The longer the melt stays in the (straight) end channel, the more the orientations are able to relax, and the lower the die-swell will be.

10.23. PVC is an amorphous thermoplastic; during the heating-up along the screw of an extruder the viscosity is, after passing T_g, still very high and it decreases only slowly. Compression of the mass must, therefore, take place over a considerable part of the screw length. PA, on the contrary, is slightly above its T_m already a relatively low-viscous fluid (also since its molar mass is not very high). The compression zone may, therefore, be short.

10.24. Structural foam (or integral foam) is a foam where the walls are solid. Advantages:

- Though its production, e.g. in an injection moulding machine, requires special tricks, the injection pressures and the mould clamping forces required are much lower than with a solid product.
- The surface is, compared with a normal foam, smooth.
- The product is considerably lighter than a solid product (e.g. half).
- The solid skin provides extra bending- and buckling resistance.

10.25. *a*. blow extrusion,

b. casting of monomer (caprolactam) and in-situ polymerisation,

c. sheet extrusion, followed by vacuum forming, or rather SPPF slightly below T_m.

d. injection moulding,

e. calendering and cutting,

f. centrifugal casting from a paste, followed by vulcanisation,

g. calendering,

h. compounding, extrusion, moulding, vulcanisation,

i. film extrusion (balloon), cutting, welding,

j. pre-foaming of pentane containing beads, final foaming in the mould,

k. moulding, vulcanisation,

l. moulding and vulcanisation, or: injection moulding and vulcanisation,

m. sheet extrusion or calendering, thereafter sheet forming (vacuum or with extra help),

n. casting from monomer, in-situ polymerisation,

o. wire-coating extrusion round a copper wire,

p. extrusion,

q. impregnating of glass wires with a blend of resin and curing agent, winding round a mandrel, curing,

r. rotation moulding from powder,

s. moulding of a powdery compound, curing,

t. sheet extrusion, vacuum forming,

u. machining of a moulded block or moulding or injection moulding (i.a dependent on production size),

v. sheet extrusion, bending, welding,

w. spraying a powdery mixture of the two components and a blowing agent onto the wall; it then foams and hardens,

x. resin/curing agent blend apply to glass mat (hand-lay-up), curing,
y. injection moulding of pre-form; then blowing-up with bi-axial stretching,
z. sheet extrusion with pentane-injection, vacuum forming.