PHYSICS OF SOLID POLYMERS

Part 6: Fibers and Strong Plastics - Flexible Chain Polymers

MICROFIBRILS

When spherulitic (or row-structure) polymers are drawn beyond the yield point oriented fibres are produced (Figure 31). The transition at the "neck" is often sharp. The spherulitic and lamellar structure is completely destroyed and a new, "microfibrillar" structure is established. Before neck formation polymer chains shear and tilt within the lamellar crystals (Figure 30). At the neck, the lamellar-fibrillar "transition" occurs.

Within the microfibrils the polymer chains in the crystals lie parallel to the draw direction. The fibre is made up of "microfibrils", 10-20 nm in diameter (Figure 29). These consist of alternating crystalline and amorphous regions, with typically 10-20 nm periodicity. The small crystallites are thus typically 15 nm in width and 15 nm in thickness. They are not lamellar and have a low proportion of chain folds. There are many "tie-molecules" along the microfibril which give the fibre a relatively high axial modulus of a few GPa (compared to a fraction of a GPa in unoriented flexible crystalline polymers between their T_m and T_g).

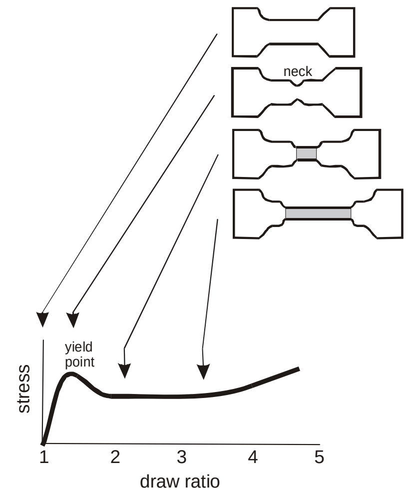


Figure 31 Drawing of a test piece of a semicrystalline polymer, showing the formation of the neck, and the corresponding stress-strain diagram

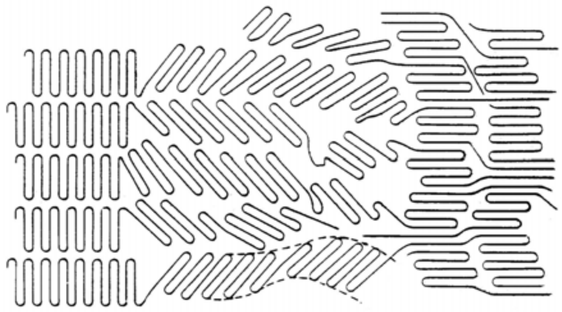


Figure 30

Schematic drawing of the transformation in the neck region during drawing, showing polymer molecules. Left: lamellar (spherulitic) morphology; middle: molecules slip and tilt within the lamellae prior to necking; right: catastrophic lamellar breakup and formation of microfibrils.

Laterally microfibrils are poorly connected and drawn fibres or films easily fibrillate.

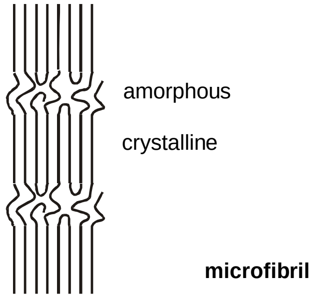


Figure 29 An individual microfibril (schematic).

FABRICATION OF CONVENTIONAL FIBRES

Fibres are spun from polymer *solution* or from *melt*. After spinning (and drying), fibres are usually *stretched* additionally and *annealed* at elevated temperature to increase their modulus and strength. Fibres are produced as *yarns* (bundles of 10^2-10^3 very long parallel filaments, several μm), *staple* (short randomly oriented filaments), and *monofilaments* (individual very long filaments, much thicker, e.g. 0.1 - 2 mm).

Solution Spinning

a) Wet Spinning

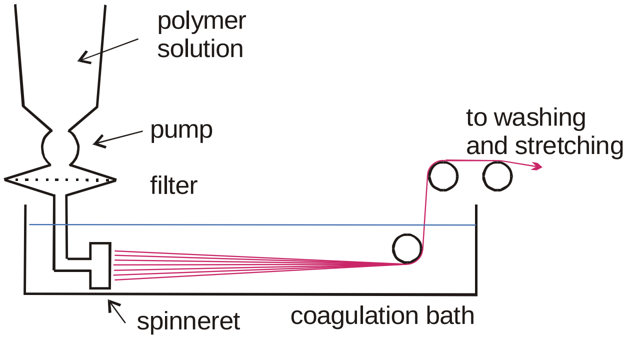
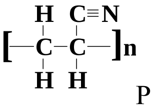


Figure 32 Industrial wet spinning process

Highly viscous polymer solution is squeezed through dies of a *spinneret* (metal plate with holes) into a poorer solvent or nonsolvent in the *coagulation bath*. The coagulated (precipitated) polymer is drawn by the pull of take-up rolls. Coagulation must not be too abrupt (grainy fibres), hence solvent is usually replaced by a mixture of solvent and nonsolvent. Individual filaments are collected in a yarn.

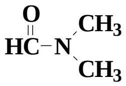
Typical systems: 1) *Viscose rayon* (cellulose regenerated from wood pulp) alkaline solution coagulated in sulphuric acid containing Na and Zn sulphate (N.B. Film of the same material is known as *celluloid*). 2) *Polyacrylonitrile* (PAN, "acrylic fibre", Orlon) solution in dimethylformamide (DMF) spun into aqueous dimethylacetamide (DMA). 3) *Spandex* (polyurethane elastomer) DMF solution spun into water.

Common solvents for wet spinning:

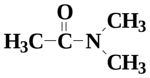


$$\left[-\overset{H}{\underset{H}{C}}-\overset{C\equiv N}{\underset{H}{C}}-\right]_n$$

PAN



DMF



DMA

Disadvantages of wet spinning: 1) slow. 2) Uneven shrivelled cross-section (core coagulates slower than skin - Figure 35d). The large surface area created could be an advantage, e.g. better moisture absorption, more comfortable to wear.

b) Dry Spinning

Concentrated polymer solution is pumped downward through filter and spinneret into a *stream of hot air* for drying. Solvent is recovered from hot air by condensation. The filaments are wound up and sent to further processing (stretching, drying, conditioning) - Figure 33. In order to use the minimum of solvent, the concentrated solution is heated to reduce viscosity. The process is faster than wet spinning.

Solvents: often highly volatile (acetone, CS_2); DMF and DMA for PAN and Spandex; water for poly(vinyl alcohol). Fibre surface area is high - Figure 35c.

c) Melt Spinning

Polymer *melt* is extruded through the spinneret into *cold air*, where it solidifies - Figure 34. Advantages: process is very fast (today e.g. up to 180 mph for Nylon) and fibre cross-section is smooth and circular, or any other shape determined by the die - Figure 35b. Note however that the fibre diameter is larger than that of the die due to "die swell", i.e. to the visco*elastic* nature of polymer melt. Disadvantage: Some polymers degrade too rapidly above the melting temperature (e.g. Nylon spun around 285°C). To prevent oxidative degradation, most processes take place under nitrogen. Biodegradable polymers produced by bacteria (Biopol) are particularly sensitive.

Typical yarns: Nylon 6 and 66, poly(ethylene terephtalate) (PET, Terylene, "polyester fibre"), polyethylene, vinyl chloride copolymers, polyurethane, PAN. PAN is plasticized with 30-40% DMA to reduce T_g.

Monofilaments: Nylon 11 and 6,10, polyethylene, polypropylene.

Glass fibres are also produced by melt spinning. Temperature 1300-1400°C.

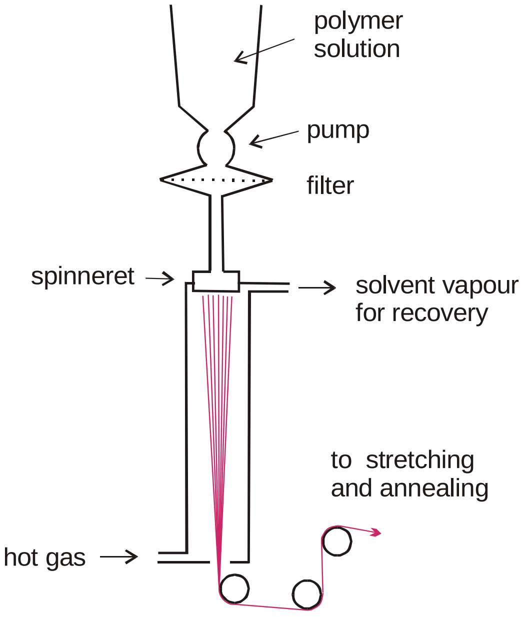


Figure 33 Dry spinning

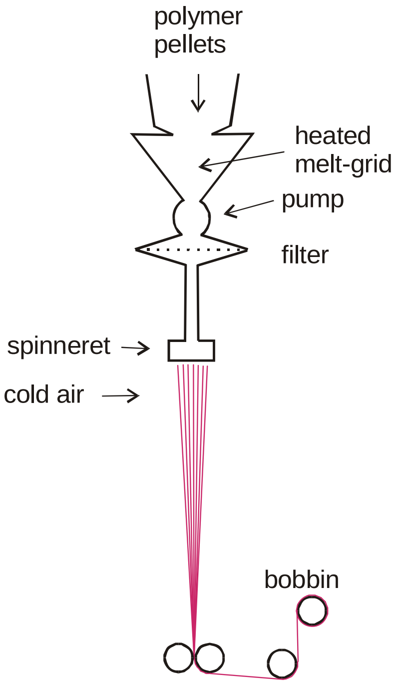


Figure 34 Melt spinning

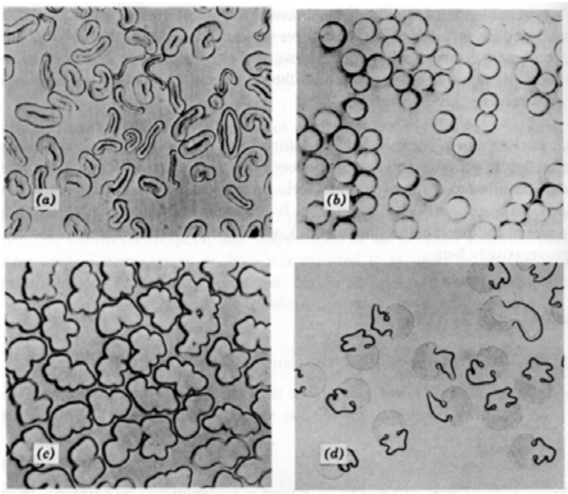


Figure 35 Micrographs of fibre cross-sections (×150): a) cotton, b) melt-spun polyester (PET), c) dry-spun cellulose acetate, d) wet-spun viscose rayon.

Post-processing

Fibres are stretched, either cold (Nylon) or at elevated temperatures (polyesters), after spinning to obtain maximum modulus and strength. Melt-spun fibres usually have row structure (cylindrites), hence have poor molecular orientation and a modulus < 1 GPa. Stretching produces a draw-ratio $\lambda = 3 - 6$, reducing the cross-section and increasing the modulus to 3 - 5 GPa. (*These values should be memorized!*). Neck is formed and the transformation to microfibrillar structure occurs (Figure 30, Figure 29). In a continuous industrial process, stretching is achieved by passing the fibre over drums rotating at increasing speed (Figure 36). Fibres must be stretched above their T_g (e.g. PET, > 100°C). Aspects of this process are technically challenging – e.g. tolerance of the gap between rollers must be a fraction of a μm.

After stretching, fibres are subjected to *sizing* (coating).

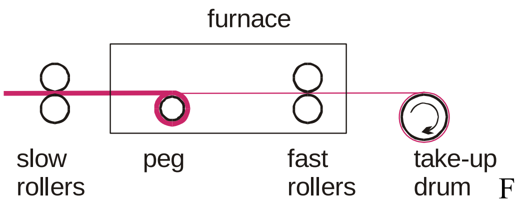


Figure 36 **Stretching of spun fibres**

Stress-strain diagrams

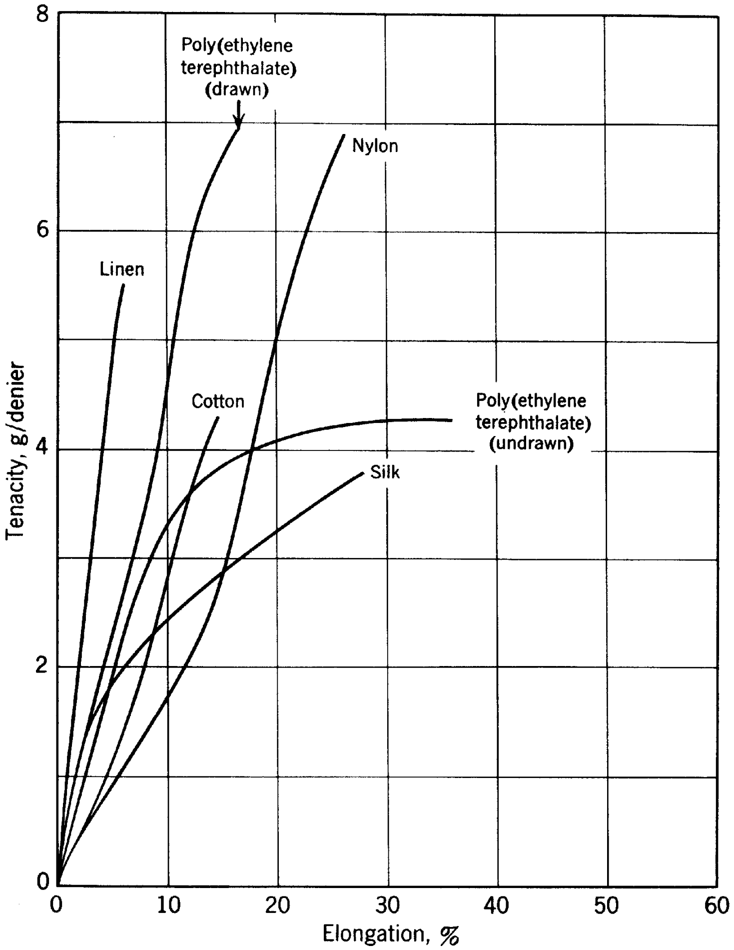


Figure 37 Stress-strain diagrams of “silk-like” fibres

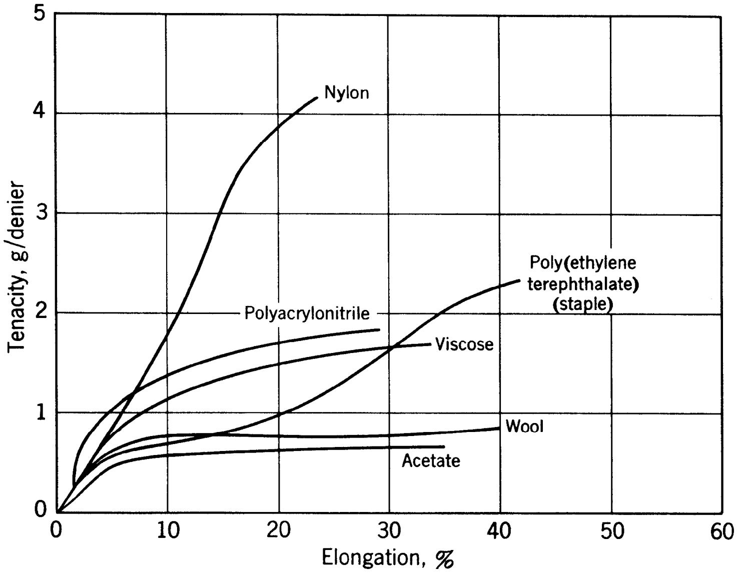


Figure 38 Stress-strain diagrams of "wool-like" fibres

Textile fibres are characterised by *denier*. Denier is the weight in grams of 9 km of a fibre. Denier is proportional to fibre density and cross-sectional area.
Tenacity is a measure of breaking strength. It is usually expressed in grams per denier.

ULTIMATE ELASTIC MODULUS OF A POLYMER

A drawn polymer fibre is a bundle of parallel microfibrils with few interfibrillar connections.

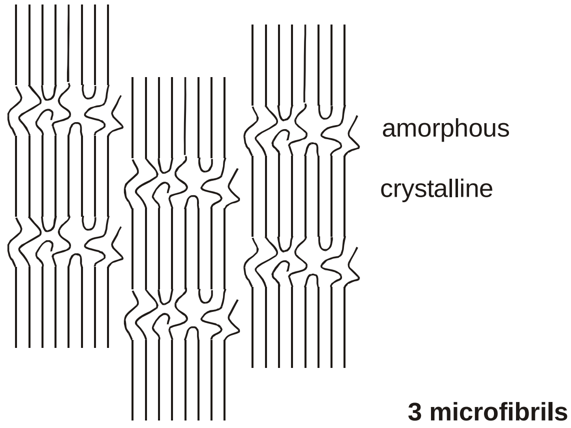


Figure 39

The mechanical equivalent of the elastic properties of such a fibre (neglecting time-dependent viscous elements) can be represented as in Figure 40.

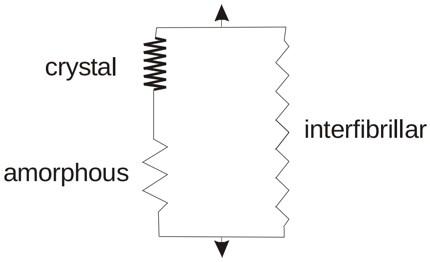


Figure 40

The stress is shared by intrafibrillar (*fib*) and interfibrillar (*int*) elements coupled in parallel, hence

$$E = E_{fib} + E_{\text{int}}$$

The low E_{int} may be neglected. Within the microfibril the hard crystalline and the soft amorphous elements are connected in series, hence their compliances (inverse moduli) add up50

$$\frac{l}{E_{fib}} = \frac{l_c}{E_c} + \frac{l_a}{E_a}$$

where l_c and l_a are the lengths of the crystalline and the amorphous segment.

It is clear that the ultimate elastic (Young’s) modulus would be achieved if the soft amorphous element was eliminated, so that the polymer chains were fully extended in the draw direction. There are several methods of determining the ultimate modulus, i.e. the crystalline modulus in the chain direction.

1. X-ray Diffraction of Strained Fibre

A fibre is gripped between jaws of a tensile testing instrument and strained. Stress is measured by a stress transducer in the usual way. However the strain is not measured by a strain gauge, since this would give E_{fib}. Instead, crystalline strain E_c (deformation of the unit cell) is determined by X-ray diffraction. Ideally the shift of an 00*l* reflection is measured. E.g. in PE this is the 002 reflection.

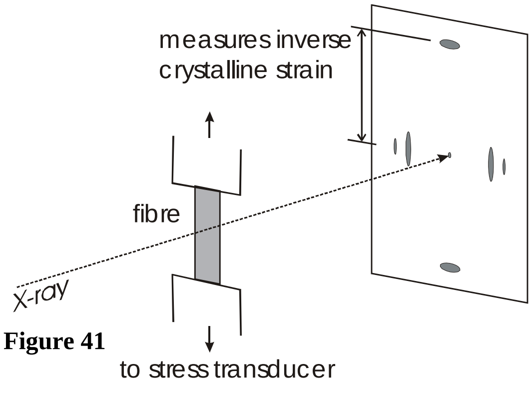
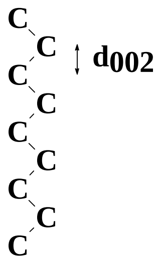


Figure 41

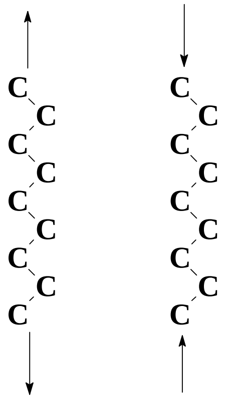


Using the Bragg equation,

$$\lambda = 2d_{002}\sin\theta_{002}$$

where λ is the X-ray wavelength, the shift in the position of the 002 reflection can be related to the strain of the zigzag chain of PE in the crystal.

2. Determination of E_c from Raman Shift of Longitudinal Acoustic Mode (LAM) Vibration



LAM (also called accordion mode) is a vibration mode where the whole extended segment of a chain oscillates longitudinally. It is inactive in IR but active in Raman scattering at very low frequencies, typically $\Delta\nu = 10 - 50\ \mathrm{cm}^{-1}$ (i.e. there are 10-50 wavelengths in 1 cm). $\Delta\nu$ is inversely proportional to the length of the vibrating straight segment l_s:

$$\Delta\nu = \frac{1}{2l_s}\sqrt{\frac{E_c}{\rho}}$$

ρ is density and E the Young's modulus of the polymer chain. The problem is equivalent to the vibration of a spring, where E/ρ is the spring constant. The best way to determine E is to measure ν_1 on a series of crystalline extended-chain n-alkanes (linear paraffins, C_nH_{n+2}), whose $l = l_s$ is well known. E is determined from the slope of ν_1 against l^{-1}.

> N.B. In Raman spectroscopy we measure the change (shift) in frequency ($\Delta\nu$) of light photons from a laser, which are inelastically scattered on a specimen. Most photons are scattered elastically (Raleigh scattering), but some give or take a comparatively small amount of energy exciting or extinguishing a molecular vibration mode.

Incidentally, for a polymer whose E has been determined, LAM spectroscopy can be used to measure the thickness of crystalline lamellae, i.e. l_s.

Problem: With the help of small-angle X-ray scattering (SAXS) and low-frequency Raman spectroscopy, how would you determine whether polymer chains are perpendicular or tilted in the crystalline lamellae?

- For PE both methods give 250 GPa < E_c < 300 GPa
- Key to high modulus:
  eliminate soft amorphous segments with chain folding
  → obtain extend chains
- An extended polymer chain can stretch further in 3 ways (in order of ascending energy cost):
  - bond torsion
  - bond angle deformation
  - bond stretching

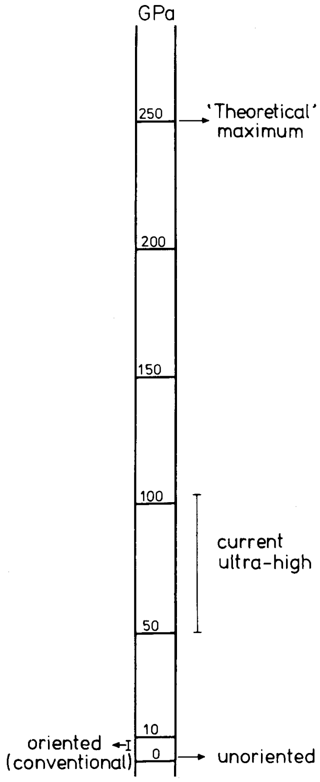


Figure 42 Theoretical and achieved modulus scale for polyethylene

The lowest E_c is expected

from polymers that can be stretched through bond torsion (e.g. helical polymers - PEO, PP etc.). Polyethylene and Kevlar are stretched mainly by bond angle opening. The stiffest polymers are those where bonds must be stretched (e.g. PBO, PBZT - lyotropic polymers, see later).

Two routes to high modulus and strength:

1. **Extend flexible chains**
2. **Align rigid chains**

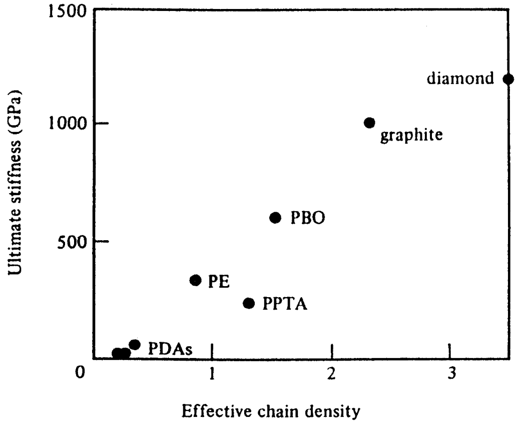


Figure 43 Theoretical moduli of stiff materials

(PPTA = poly(phenylene terephtalamide – Kevlar)
(PBO = poly(phenylene bisbenzoxazole)

CHAIN EXTENSION IN FLEXIBLE POLYMERS

The preferred polymer chain conformation in melt or solution is random coil. Spontaneous chain extension is improbable (entropically unfavourable).

High degree of chain extension is essential for high modulus. To achieve high strength and creep resistance, high molecular weight is also preferred.

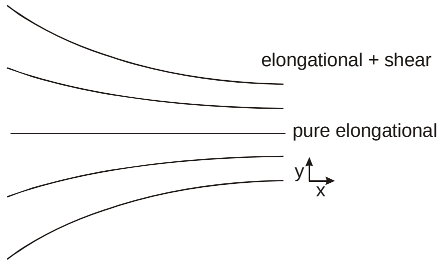


Figure 44

The best way to obtain chain extension is **extensional** (or elongational) flow. Shear flow is less effective but far more common. In extensional flow the velocity gradient is parallel to the velocity vector. In shear flow the velocity gradient is perpendicular to the velocity.

$$\text{shear}: \frac{dx}{dy} = \varepsilon \qquad \text{shear rate}: \dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{dv}{dy} \ (s^{-1})$$

$$\text{extensional flow rate}: \qquad \frac{dv}{dx} \ (s^{-1})$$

Take shear flow; the same principle applies also to extensional flow. In order that the polymer chains are prevented from coiling up, a necessary (but not sufficient) condition for effective chain extension is that the shear rate is **above a critical shear rate** $\dot{\varepsilon}_c$. $\dot{\varepsilon}_c$ is the minimum shear rate necessary to extend the whole polymer chain. $\dot{\varepsilon}_c \approx \tau_0^{-1}$ where τ_0 is the longest relaxation time of a polymer chain in a given environment. E.g. for polyethylene of medium M_w in a dilute solution $\dot{\varepsilon}_c = 10^3$ s^{-1} (this means moving two plates separated by 1 inch of solution at 70 mph with respect to each other!). If $\dot{\varepsilon}$ is below $\dot{\varepsilon}_c$, polymer chains will not extend or, if an extended chain is introduced, the flow will not sustain the extended conformation; the chain will relax (coil up).

τ_0 is the longer (and $\dot{\varepsilon}_c$ the lower) the higher the molecular weight, the more rigid the polymer, the lower the temperature, and the higher the viscosity.

In order to preserve chain extension after the cessation of shear, polymer conformation must be frozen (τ_0 increased to infinity) either through crystallization or vitrification while still under shear. This means that it is impossible to makes extended chain fibres of flexible polymers by spinning from dilute solutions or melt.

At the other extreme, i.e. long τ_0 and low $\dot{\varepsilon}_c$, is the case of solid polymer subjected to cold drawing. While preservation of achieved extended chain conformation would pose no difficulty here, the problem is now with the very low rate of chain extension due to long τ_0. In practise only ***short segments*** of the polymer chain succeed in rearranging (extending) in cold drawing, their relaxation time τ_s being shorter than that of the whole chain (τ_0) and commensurate with the time scale of the drawing process. Therefore, in a cold-drawn fibre or film, only segments of average length *s* are extended, spanning one or several crystal lengths. The overall chain conformation is still only an **elongated random coil**.

It appears that the "extendable segment length" l_s limits the drawability to the "**natural draw ratio**", typically 4-10. A particular obstacle in the way of full chain extension in solid and molten polymers is the presence of ***physical chain entanglements.***

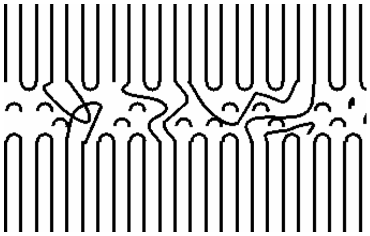


Figure 45 Amorphous layer in a melt-crystallized polymer

Figure 30 shows the chains being pulled out of solution-grown single crystals which have few chain entanglements. However, in bulk (melt-crystallized) polymer, the fold surface is less regular and there are many entanglements in the amorphous phase (Figure 45). These cannot be all undone in the drawing process in the solid state. The result is incomplete chain extension, which means that there are many folded and loose chains in the amorphous phase of cold-drawn polymers. Accordingly, the modulus does not exceed a few GPa, a small fraction of the theoretically achievable E.

Summary:

- *If achieved, extended polymer conformation must be frozen in*
    - *by **crystallization**, **vitrification** or **coagulation**.*
- *To prevent chains recoiling at low / moderate* $\dot{\varepsilon}$*, we need long* τ_0.
    - *This is achievable by:*
        1. *drawing or extrusion in the **solid state,** or*
        2. *drawing of **UHMW** polymer solution (gel).*

Ultradrawing

Where the draw ratio λ is increased successfully beyond the "natural draw ratio", it was found that $E \propto \lambda$ - see Figure 46

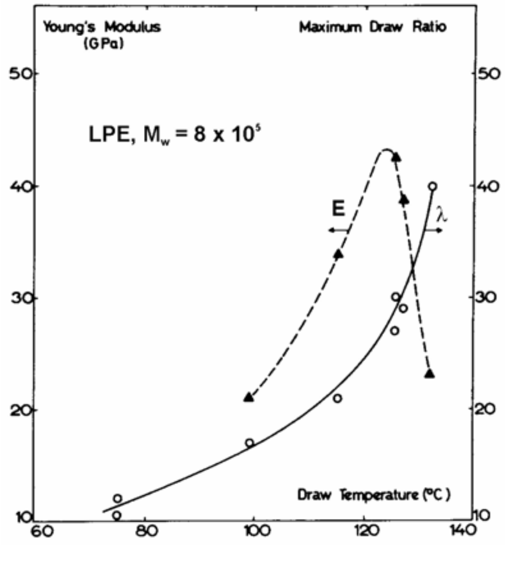


Figure 46 Linear relationship between Young's modulus and λ for ultradrawn linear PE

Goal: increase λ !

How?

- Disentangle chains more effectively

"Ultradrawing"

- draw at elevated temperature
- often 2 or 3 stages
    - first at lower, then at higher T

- The higher the temperature, the shorter the relaxation time τ, and the longer the extended segment length l_s for a given shear rate $\dot{\varepsilon}$.

As drawing temperature is increased, l_s increases; hence chains disentangle.

But:

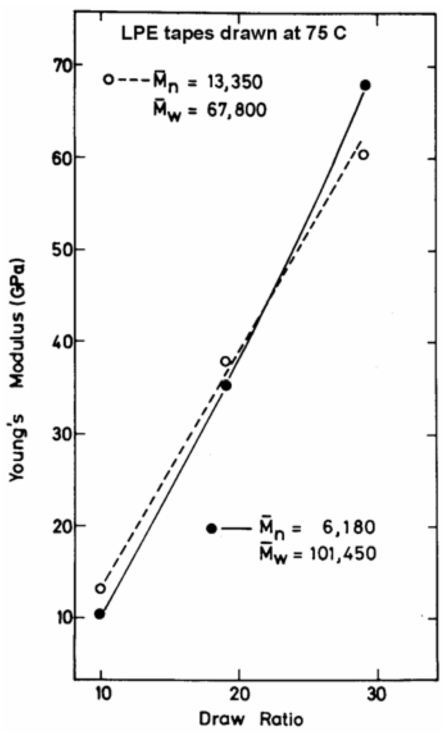


Figure 47

As T increases - $\dot{\varepsilon}_c$ also increases
(chains recoil faster)
→ above 120^{o}C, i.e. a few °C below melting point of PE, chain extension cannot be sustained
using the shear rates ε normally used in drawing

→ resulting *E* decreases.

(In spite of this λ can increase almost indefinitely – think of drawing honey).

The reason that the maximum achievable λ decreases with Mw is that **e**ntanglements are more difficult to eliminate. However, the solution is not in reducing Mw; this would reduce fibre strength, and below a certain Mw the material would break and not be ductile at all.

The reason that slowly crystallized polymer can be drawn to larger λ than quenched one is that the former contains
fewer entanglements.

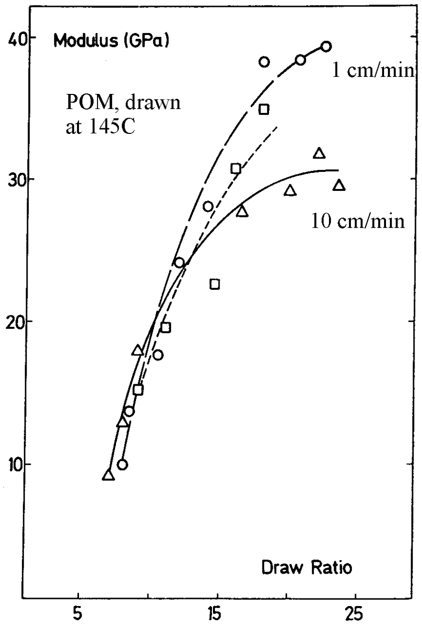


Figure 49 E vs. λ for ultradrawn poly(oxymethylene) (“polyacetal”)

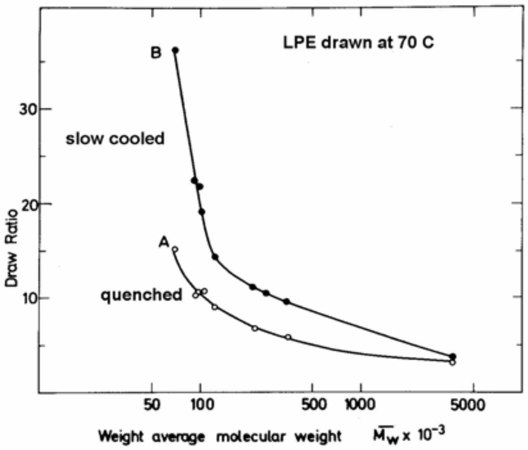
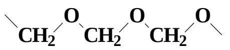


Figure 48 Effect of weight-average molecular weight and crystallization conditions on ultimate λ

Polymers other than polyethylene can also be ultradrawn to achieve high modulus. Polyoxymethylene (POM) and i-PP can also be ultradrawn. Figure 49 illustrates this for POM (“acetal resin”, “polyacetal”).



$-CH_2-O-CH_2-O-CH_2-O-$

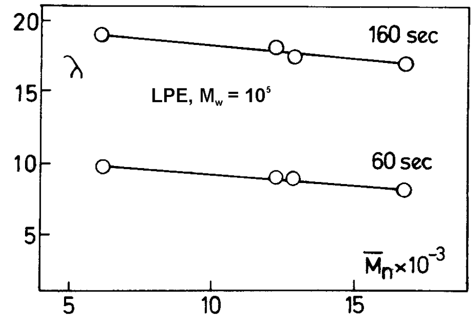


Figure 50

As Figure 50 shows, for a given M**w**, λ is independent of M_n (the number-average molecular weight).

Figure 50 also shows that slower drawing leads to higher λ.

However note:

1. 10 000 is a very low M_w
2. The drawing in Figure 50 is very slow.

In spite of these limitations ultradrawing is being commercialized for the production of special fibres. Strong fibres of flexible polymers can be obtained faster and with higher modulus by "gel-spinning" (see later).

Solid State Extrusion

Thick rods and tubes of different profiles, having high modulus (and transparency!) can be obtained by extrusion of polymers in the solid state.

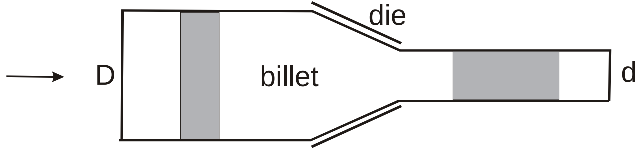


Figure 51 Principle of solid state extrusion

Solid state extrusion is equivalent to drawing. The draw ratio is equivalent to the ratio of cross-sections before and after extrusion.

$$R_A = \lambda = D^2/d^2$$

For PE, Youngs moduli in the range 20 - 50 GPa can be achieved in this way.

In practice, solid state extrusion is carried out by (a) **ram extrusion,** (b) **hydrostatic extrusion** and (c) **die drawing**.

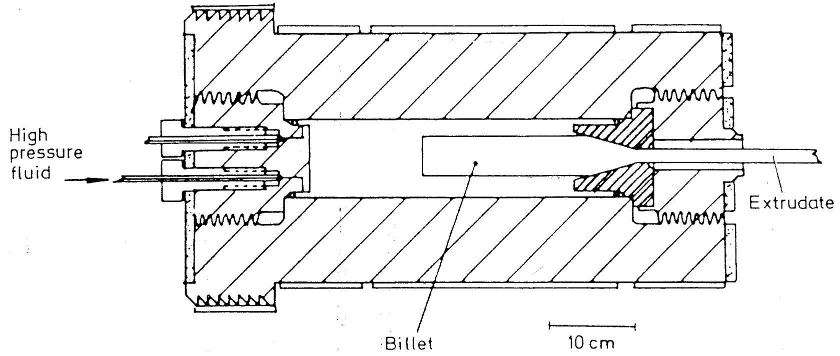


Figure 52 Hydrostatic extrusion

In ram extrusion a crossbar forces a polymer billet through the die. Hydrostatic extrusion has the advantage over ram extrusion in that the billet is pressurized evenly rather than unidirectionally, avoiding bending or fracture. Much lower force is needed to create the required pressure, and the hydraulic oil acts as a lubricant. The advantage of die drawing over hydrostatic extrusion is in that the billet can be heated, increasing the drawability, and that oil can be avoided, reducing contamination. The natural shape of the neck is such that friction with the die is minimised. The drawn material must have sufficiently high strength and modulus for die drawing to be possible.

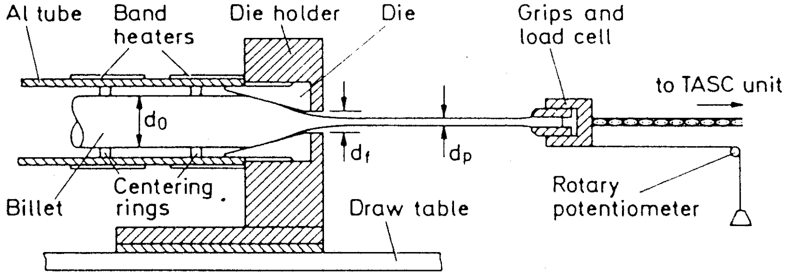


Figure 53 Die drawing

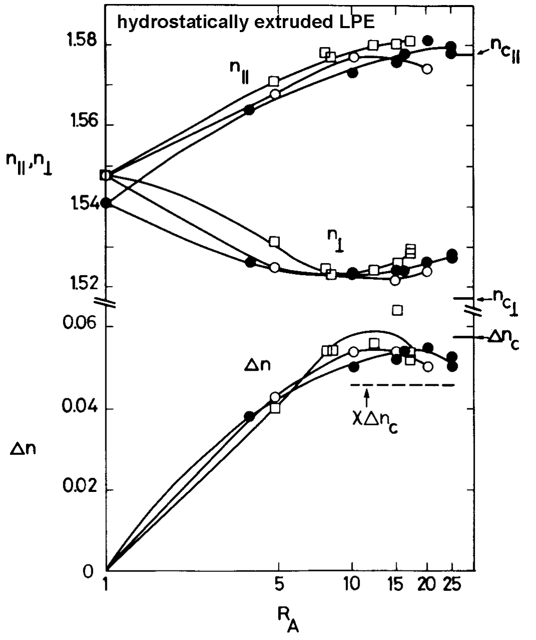


Figure 54 Effect of axial ratio (= draw ratio) on birefringence. $n_\parallel$ ($n_\perp$) = refractive index of light polarized $\parallel$ ($\perp$) to extrusion axis.

Figure 54 shows the dependence of the two refractive indices $n_\parallel$ and $n_\perp$, and of birefringence $\Delta n = n_\parallel - n_\perp$ on draw ratio. n_c and Δn_c refer to the contribution of the crystalline fraction, with perfect orientation of chains along the extrusion direction. In cases where $\Delta n > X\,\Delta n_c$ (X is crystallinity), the excess $X\Delta n_c$ comes from the preferred chain orientation in the amorphous phase. This amorphous orientation, indicating taut tie molecules, is crucial for high modulus.

Ideally, to achieve both maximum strength and maximum modulus, a polymer chain should have just one entanglement. This would enable transfer of stress (high strength) and at the same time leave the rest of the chain to be extended and fully crystalline (high modulus). High molecular weight is required for high strength (reduction in number of chain ends). However, high MW usually means high number of entanglements per chain. There are two ways around this problem, using solution at some stahe.

Drawing of Solution-Grown Single Crystals

Since molecular chains are regularly folded in single crystals of polymers such as PE (Figures 2,3), there are few entanglements (Figure 30) and drawing at elevated temperatures can produce extended chains. Molecular weight must be high (e.g. 400,000), otherwise the mats will crack. The solution from which the crystals are precipitated is, ideally, "semi-dilute" (e.g. 1%). This allows some molecular (covalent) links between individual crystals. Too low a concentration means that most chains belong entirely to one crystal; too high a concentration means too many entanglements. In fact drawing single crystal mats still produces fibres and tapes of the highest achievable modulus and strength in flexible polymers - see Figure 55. However, the process of drawing single crystal is not commercially viable.

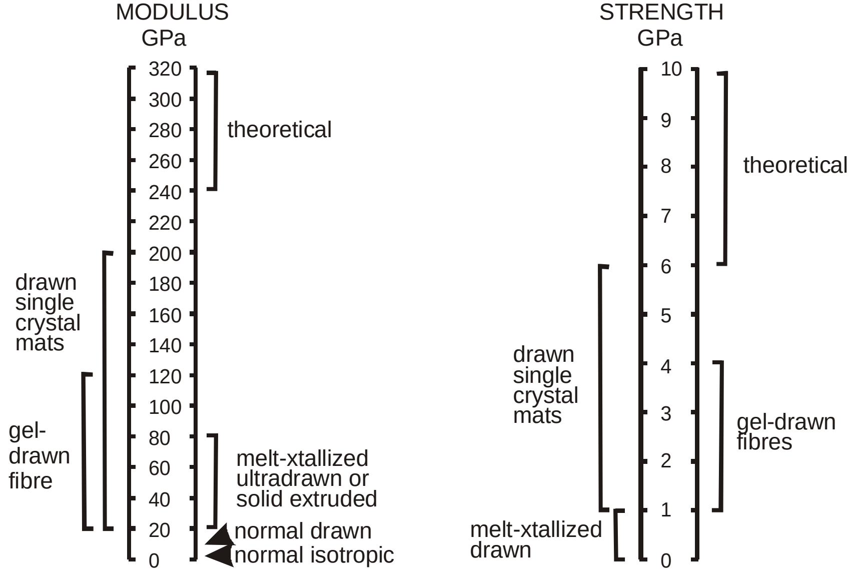


Figure 55

Gel-Spun Fibres of UHMW PE

Ultra-high molecular weight polyethylene (UHMWPE):

τ_0 is very long, hence $\dot{\varepsilon}_c$ is reasonably low to be achievable under industrial conditions

- UHMW = 1 – 6 million Daltons (typically 3 M)
- commercial: Hostalen GUR (Hoechst, Germany), Hizex (Japan)
- quenched concentrated solution (1-3%) → turbid gel (contains some chain-folded single crystals)
- at higher T (> 100^{o}C) → clear gel (Figure 56)
- solvent: decalin (high boiling point)

The drawing speed of gel must be such that $\dot{\varepsilon} \approx$

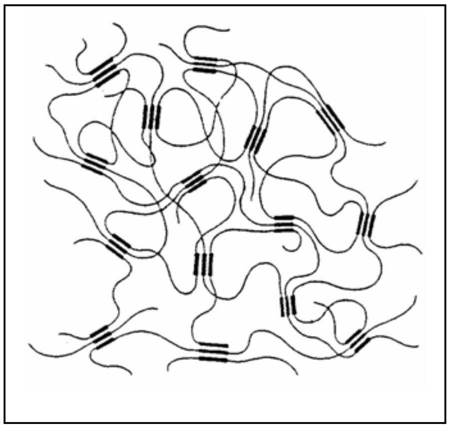


Figure 56 Schematic structure of clear UHMWPE gel. 1-3% solution in decalin or kerosene. The 10-20 nm "fringed micelle" crystallites act as physical crosslinks.

$\dot{\varepsilon}_c \approx 1/\tau_0$. If $\dot{\varepsilon}$ too high – breaking of chains (If $\dot{\varepsilon}$ too low – possible recoiling). This limits the speed of the process.

The essential advantages of this process are:

- Presence of solvent **removes chain entanglements** and allows full chain extension (unlike in solid-state extrusion).
- The high molecular weight and the physical crosslinks prevent recoiling of the extended chains ($\tau_c \rightarrow \infty$) (unlike in wet, dry or melt spinning).

– **drawing induces extended-chain crystallization**

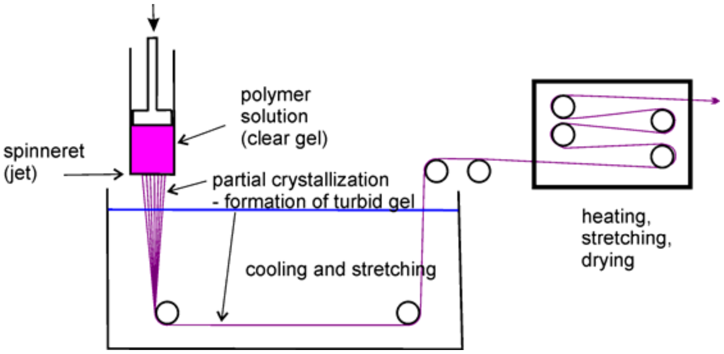


Figure 57 Continuous gel-spinning process

Resulting fibres have

- modulus up to **120 GPa** (1/2 theoretical E)
- strength up to **4 GPa** (on a weight basis this is 10 times higher than steel!) – this is still only 1/6 of theoretical strength (stress required to break C-C bond). Shortfall due to defects.
- elongation at break ≈ 4%, theoretical: 32%. Shortfall is due to defects.
- commercial *continuous* gel-drawing process
  - patented by DSM (Netherlands) (Smith and Lemstra)
- manufactured by
  - Honeywell (formerly Allied Signal) as "Spectra"
  - by DSM as "Dynema"

- **Applications of gel-spun UHMWPE fibres:**
  - marine rope, fishing line, sail reinforcement
  - protective gloves (for surgeons, workers handling glass, metal sheets)
  - bullet-proof vests
  - protective shields (2 or 4 layers of non-woven fibres, oriented at 90^o, embedded in resin); useful in aerospace for their ultralight weight.
  - not suitable for high-temperature applications (melting point 130°C)

(see www.honeywell.com for application of Spectra fibres)

Gel-spinning of other polymers

Of all flexible polymers, PE has the highest theoretical modulus (e.g. i-polypropylene is a helix – on stretching gauche bonds turn to trans, which requires less energy than bending C-C-C bond-angle in polyethylene). Also PE chains slide easily past each other in the crystal, since there are only weak van-der-Waals intermolecular forces. However, this is also the reason that gel-spun PE fibres suffer from creep on prolonged loading. Other gel-spun fibres include POM (polyoxymethylene) and poly(vinyl alchohol).

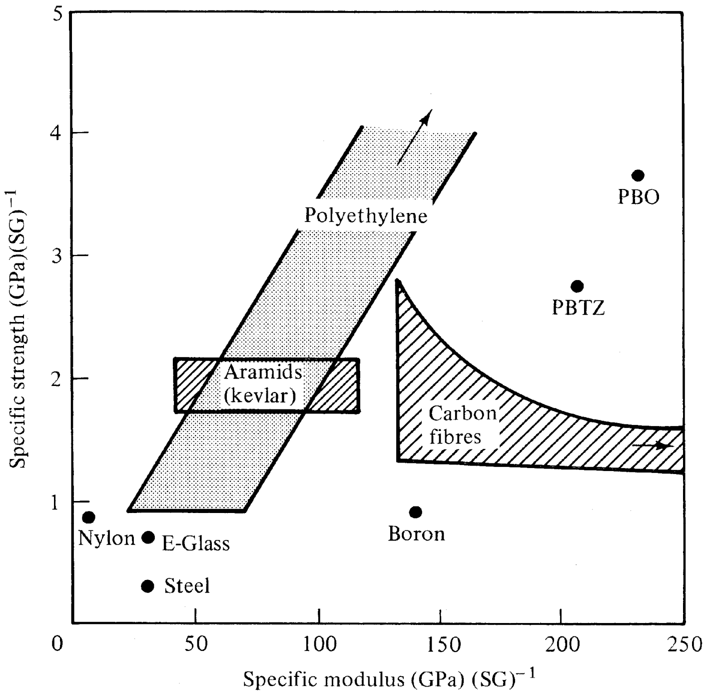


Figure 58 Specific strength and modulus (i.e. values per unit density) of high-performance polymer fibres and related materials (note: SG = specific gravity)