CHAIN-EXTENDED FLEXIBLE POLYMERS

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SUMMARY

High-strength/high-modulus structures such as fibres, tapes and rods can be produced currently on the basis of intrinsically flexible macromolecules. The prime example amongst these new developments is gelspinning of high-molecular-weight polyethylene resulting in fibrous structures possessing tenacities of 3-4 GPa and corresponding moduli up to appr. 150 GPa. The basic aspects of chain-extension for polyethylene will be discussed in relation to the various routes toward oriented/extended PE structures as well as recent developments concerning the utilization of other flexible polymeric systems for the production of high-strength/high-modulus fibres.

INTRODUCTION

The development of high-strength/high-modulus organic fibres is following two routes which are completely different with respect to the starting materials, respectively intrinsically rigid vs. intrinsically flexible macromolecules.

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Rigid chains

Chain-extension/alignment, a prerequisite for obtaining high-strength/high-modulus structures, is achieved relatively easily in the case of intrinsically rigid macromolecules in comparison to their flexible counterparts. Of course, this statement does not apply to the sophisticated chemistry which is necessary to synthesize rigid chain macromolecules. The prime examples of "rigid chain" polymers are the aromatic polyamides (aramids) notably PPTA (poly-p-phenylene-terephthalamide), well known under the trade names of the corresponding fibres Kevlar (DuPont) and Twaron (Akzo/Enka), possessing tenacities of appr. 3 GPa and corresponding moduli up to 130 GPa. Although the aramids are not strictly rigid in the sense that the individual molecules in dilute solution behave like "rigid rods"\(^1,2\), experimental conditions have been found such as spinning from liquid-crystalline (nematic) solutions which promote chain-extension/orientation along the fibre-axis.

A possible advantage with respect to the spinning procedure might be offered in the form of the new class of aromatic polyester polymers, in which case melt-spinning is possible, resulting – as claimed recently\(^3\) – in high-performance fibres.

Flexible chains

In contrast to spinning of "rigid chain" systems, flexible (regular) chains tend to fold during solidification. Consequently in conventional spinning operations the formation of folded-chain type crystals is unavoidable during some stages of the spinning-operation such as during cooling of for example a polyamide or polyester melt (melt-spinning), solvent-evaporation (dry-spinning) or solvent-extraction/coagulation (wet-spinning) of for example polyvinylalcohol. The transformation of these folded-chain type crystals into chain-extended structures via postdrawing techniques of yarns, in a temperature range close to but below the melting point, is not adequate if a comparison is made between the axial moduli of currently large-scale manufactured technical yarns such as nylon-6, polyester and polyvinylalcohol with their predicted theoretical limits, shown in Tab. 1.
Tab. 1. Young's moduli, comparison between theoretical limits and actual values.

<table>
<thead>
<tr>
<th>Material</th>
<th>E_{theor}* (GPa)</th>
<th>E_{practice} (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyester</td>
<td>120-150</td>
<td>20</td>
</tr>
<tr>
<td>polyamide (nylon-6)</td>
<td>170-250</td>
<td>6</td>
</tr>
<tr>
<td>polyvinylalcohol</td>
<td>200-250</td>
<td>30</td>
</tr>
</tbody>
</table>

* data taken from references 4,5

During the past ten years much progress has been made in understanding the paramount factors controlling the transformation of folded-chain type crystals into chain-extended structures. It should be admitted that these developments are rather confined to polyethylene, as will be discussed below, but the impact on other flexible polymeric systems will be evident in the near future as discussed in the section "other flexible polymers".

CHAIN-EXTENDED POLYETHYLENE

Linear polyethylene has always been the prime model substance in studying the crystallization behaviour of polymers in relation to morphology. Since the discovery in the mid-fifties of folded-chain type PE crystals as grown from dilute solutions 6,7,8,9, numerous papers have been devoted up to now to the detailed chain topology of PE within, and at, the boundary of the crystals. Fortunately not every polymer scientist led himself be carried away in endless debates about minor details of chain topology but already in the early sixties attempts were made to induce chain-extension/orientation using PE as a model substance. In fact in the sixties, elementary findings were made such as stirring of supercooled solutions resulting in fibrous structures 10 and the important observation that single crystal mats of polyethylene are remarkable ductile 11. It is beyond the scope of this paper to review in chronological order the various contributions which were made in the past to obtain chain-extended PE (for a detailed discussion the reader is referred to ref. 12). However, to understand the paramount factors involved, a brief survey is given of various routes towards chain-extended polyethylene.
Chain-extension in dilute PE solutions

In general to change the conformation of a (flexible) macromolecule from a random coil into an extended-chain conformation, the following conditions should be fulfilled 13:

\[ \dot{\varepsilon} \cdot \tau >> 1 \quad \dot{\varepsilon} \cdot \Delta t >> 1 \] (1)

In equation (1), \( \dot{\varepsilon} \) is the rate of strain, \( \tau \) the conformational relaxation time and \( \Delta t \) the time during which the macromolecule is exposed to the flow field. In the case of flexible macromolecules such as polyethylene and polystyrene, the conformational relaxation times in dilute solutions are very short, typically in the order of \( 10^{-3} - 10^{-5} \) seconds depending on the molar mass 14,15. Consequently, special devices are necessary to induce chain-extension in order to generate the proper (elongational) flow field at a corresponding high rate of strain. These requirements are not compatible with any technological process, but demonstrate the intrinsic difficulty of inducing chain-extension in the case of flexible macromolecules in dilute solutions.

Relaxation times of macromolecules in concentrated systems, in particular melts, are much longer compared to those in solutions. Consequently, chain-extension is expected to be easier, especially with high-molecular weight, and the use of strong elongational flows at lower temperatures. However in the case of linear polyethylenes it is nearly impossible to preserve chain-extension in the melt into the solidified product. Only in supercooled melts, chain-extension of the high-molecular-weight part, can be made permanent due to strain-induced crystallization. This processing method is rather critical, if the temperature is too low capillary blocking occurs 16 and with increasing temperatures the mechanical properties of the spun/quenched fibres deteriorate due to relaxation processes 17.

However, chain-extension can be made permanent and obtained relatively easily in the case of supercooled solutions of UHMW-PE (ultra-high-molecular-weight polyethylene). The long chain macromolecules constitute an entanglement-network and consequently due to this entanglement-coupling the conformational relaxation times are reduced considerably and even in weak shear flows, chain-extension can be made permanent as result of nucleation and
alignment/crystallization of (partly) oriented chains.

It was demonstrated by Zwijnenburg and Pennings 18 about 10 years ago that from the surface of the inner rotor in a Couette-type apparatus, PE structures with exceptional properties could be pulled away in the case of supercooled UHMW-PE solutions. Figure 1a shows the experimental set-up of this so-called surface growth process. In fact the surface growth process demonstrated the possibility that on the basis of UHMW-PE ultra-strong/stiff structure could be produced viz. tenacity 3-4 GPa and corresponding moduli over 100 GPa. However, the slow fibre take-up speed, typically < 1 m/min was prohibitive for any further commercialization.

Recently Mackley 19 improved and extended this technique by controlled mechanical shearing of semi-dilute UHMW-PE solutions, see Figure 1b. By shearing supercooled UHMW-PE solutions, tape like PE structures can be produced possessing stiffness values of appr. 60 GPa at take-up/roll-off speeds of several meters/min. The belt, see Figure 1b, increases the local shear rate and drags the produced tape from the surface of the rotor. Although the linear take-up speed is still not impressive compared to conventional fibre/tape wind-up speeds, the width of the tape is in principle unlimited and hence the mass of tape per unit of time could be of technological/commercial interest.
Deformation of the solid state

The conformational relaxation times of PE molecules are reduced by orders of magnitude in the solid-state in comparison with solutions and melts. Consequently on the time-scale of, for example a simple tensile drawing experiment, chain-extension can be made permanent. In the case of polyethylene it has been shown already by Statton in 1967 that folded-chain crystals are ductile and unfolding as such is achievable. Ward and coworkers studied systematically melt-spinning/drawing of linear polyethylene. By optimized post-drawing procedures of the as-spun/crystallized yarns, PE fibres could be produced continuously, possessing tenacities of about 1 GPa and corresponding moduli up to about 75 GPa. In terms of specific values for strength/stiffness these values exceed those for glass and steel, see Figure 3 below.

Melt-spinning/drawing of PE however encounters two major limitations with respect to the molecular weight, the upper limit being appr. $3 \times 10^2$ kg/mole.

The first, rather obvious limitation, is the strong increase of the melt-viscosity with increasing $M_w$ which becomes prohibitive for continuous in-line melt-spinning of yarns.

The second limitation is the decrease in drawability of the solidified melt-crystallized polyethylene. This implies that even if spinning conditions could be found to process high-molecular-weight polyethylene, the second equally important step of post-drawing would not be feasible to the required extent. In this post-drawing step the chain-folded crystals are transformed into chain-extended fibrous structures and in the case of linear PE the maximum values of $\lambda_{\text{max}}$ ($= 1/l_0$) typically drop below 10 for $M_w$ approaching $10^3$ kg/mole.

This second limitation is less obvious than the first one since there is not direct reason why the macroscopic draw ratio should decrease with increasing chain dimensions. Assuming affine deformation one would expect $\lambda_{\text{max}}$ to lie typically between:

$$\frac{1}{8} < \lambda_{\text{max}} < 0.086 M^{0.5}$$

(2)
In equation (2) the lower limit is the ratio of the fold-length (1) / chain-diameter (6), about 30-40 in the case of regularly folded-chain PE crystals and the upper bound is the maximum draw ratio of a random coil PE chain, for further details see ref. 21.

**Gel spinning**

At the end of the seventies it was found at DSM-Research that spinning from semi-dilute solutions of UHMW-PE renders as-spun gel-like filaments which were superdrawable. The prime observation was and still is that even after complete solvent removal from the as-spun/quenched filaments, via extraction and/or solvent evaporation, the generated structures still exhibited ultra-draw characteristics. The enhanced drawability in comparison with melt-crystallized UHMW-PE is reflected in the properties of the drawn structures viz. tenacities > 3 GPa and corresponding moduli > 100 GPa. The essence of this so-called gelspinning-process is that the constraints encountered in drawing melt-crystallized UHMW-PE, \( \lambda_{\text{max}} < 10 \), are removed via dissolution and solution-spun/cast structures are ultra-drawable even after complete solvent removal.

In recent years a major technological progress has been made with respect to the preparation and handling of UHMW-PE solutions. It is well-known that dissolving UHMW-PE, even in dilute solutions, is extremely difficult, the more so if homogeneous spinnable solutions are required.

Presently it is possible to prepare via continuous extrusion, see Figure 2, homogeneous solutions of UHMW-PE which implies that solution-spinning/drawing (gelspinning) is established as a viable technological process. PE-fibres possessing exceptional properties can be produced continuously, see Figure 3 (HP-PE).
Fig. 2. Continuous extrusion/gelspinning.

Fig. 3. Properties of Fibres ("Ekonol" is aromatic polyester, see ref. 3).
Apart from fibres, this new technology opens the possibility to produce continuously tapes and films both uniaxially and biaxially drawn, based on UHMW-PE's. Summarizing, the intractable UHMW-PE polymers which are used up to now only in sintering or modified ram-extrusion processes, due to their high melt-viscosity, can form the starting materials for an interesting class of new products ranging from strong/stiff fibres to high-performance tapes and films.

The role of the solvent is less obvious than might be envisaged at first sight. As mentioned above, melt-spinning/drawing of polyethylene becomes increasingly difficult with increasing molecular weight. Solvent will reduce the melt-viscosity but above all removes the "constraints" in the solidified solution-spun structures with respect to drawability. The drawability is related to the polymer concentration in solution and consequently, depending on the properties of the end-product one wants to obtain, the polymer concentration, rather than the molecular weight as in melt-spinning, sets an upper limit to the process.

BASIC ASPECTS

The drawing behaviour of UHMW-PE is characteristic for this particular class of (linear) polyethylenes and is demonstrated nicely in isothermal drawing experiments.

Figure 4a shows the maximum draw ratio $\lambda_{\text{max}}$ as a function of temperature. In this case Hostalen-Gur 412 (Hoechst/Ruhr Chemie) was used, $M_w = 1.5 \times 10^3$ kg.mole$^{-1}$. The samples were compression-moulded (M) or solution-cast (S). The solution-cast films, cast from PE/decalin solutions 2% w/v, were dried and last traces of decalin were removed via extraction with methylene chloride.

Three temperature regions can clearly be discerned:

1. In this temperature region, below $T_m^1$, the melting point of lamellar PE crystals, the drawability is strongly related to the initial polymer concentration in solution. For comparable experimental conditions (quenching of solutions) $\lambda_{\text{max}}$ is related to the polymer concentration in solution as published previously, by:

$$\lambda_{\text{max}} \sim \phi^{-0.5} \quad (2)$$
4. ISOTHERMAL DRAWING - BEHAVIOUR OF UHMW-PE.
Figure 4b shows the corresponding stress-strain curves for region-1 (note the indication 1) and the resulting properties: Young's modulus at room temperature vs. draw ratio \( \lambda \), are shown in Figure 4c. The striking difference with respect to drawability in the solid state (below \( T_m^1 \)) between melt-crystallized (compression-moulded) UHMW-PE and the solution-cast material of identical chemical composition, has been explained before \(^{26}\) in terms of a difference in intermolecular chain topology related to the two modes of crystallization. Upon dissolution of UHMW-PE, the long-chain molecules disentangle about proportional to the inverse of the polymer concentration. Consequently upon crystallization from solution this situation is reflected in the as-spun/cast (quenched) fibres or films. Figure 5 shows schematically the chain topology in UHMW-PE and its dependence on crystallization conditions.

![Fig. 5. Chain topology as a function of crystallization conditions: a) melt-crystallized; b) crystallized from solution \( \phi > \phi^* \) and c) crystallized from dilute solutions \( \phi < \phi^* \).](image)

Fig. 5. Chain topology as a function of crystallization conditions: a) melt-crystallized; b) crystallized from solution \( \phi > \phi^* \) and c) crystallized from dilute solutions \( \phi < \phi^* \).
Crystallization from (semi-)dilute solutions induces a favourable morphology for ultra-drawing (PE folded-chain crystals are ductile and unfold upon deformation, ref. 11). Trapped entanglements which could act as "constraints" (physical crosslinks) on the time scale of the drawing experiments are removed (due to disentangling in solution) to such an extent as to provide sufficient coherence between individual crystals but not to resist deformation. The role of the solvent is to generate this optimum structure for ultra-drawing but once the loose network of inter-connected lamellar crystallites is obtained the solvent can be removed (extraction, evaporation) provided that the system is not heated above the melting point, see below.

In region-2, above \( T_m^1 \) (= appr. 135°C), deformation during isothermal drawing starts from an isotropic melt. Depending on the rate of strain and molecular weight during deformation, strain-induced crystallization takes place. In the case of the long-chain PE macromolecules (UHMW-PE) the conformational relaxation times are sufficiently long in order to perform drawing experiments at experimentally accessible rates of strain \( (10^{-2} < \dot{\varepsilon} < 1 \text{ s}^{-1}) \). Figure 4 (a, b and c, note the indication 2) shows the experimental values of \( \lambda_{\text{max}} \) (4a), the stress-strain curves (4b) and the resulting properties of the drawn materials after cooling (under stress) to and measured at room temperature (4c). These stress-strain experiments were performed using a Göttfert Rheostrain at a constant rate of strain of 0.1 \( \text{s}^{-1} \).

A persistent difference is usually observed between melt- and solution-crystallized UHMW-PE during drawing in region-2, but the most characteristic observation is the upper limit at a temperature of \( T_m^2 \), appr. 155°C. This temperature is characteristic of (UHMW-PE) and reflects the upper limit for drawing experiments. At this temperature a solid-solid transition occurs (orthorombic + hexagonal) and deformation above this temperature, \( T_m^2 \) in Figure 4, is impossible due to necking and sample breakage.

An important observation is the large difference between region 1 and region-2 with respect to the efficiency of draw, see Figure 4c. In region-1 the Young's modulus of the drawn material (fibre, tape) increases strongly and continuously with
increasing draw ratio $\lambda$. In region-2 the efficiency is reduced considerably related to relaxation of (probably) the lower molecular fraction during drawing.

3. Above $T_m^2$ no (isothermal) drawing is possible due to failure of the sample at low strain. The chains in the hexagonal phase above $T_m^2$ do not withstand the applied stress and chain slippage occurs.

In continuous drawing operations of UHMW-PE, the temperature regions 1 and 2 are usually not observed. During drawing, the melting temperature of the fibre $T_m^f$, increases gradually from $T_m^1$, the melting point of lamellar folded-chain crystals, towards the upper limit $T_m^2$, the melting point of chain-extended PE under tension. $T_m^f$ depends on the draw ratio c.s. extent of transformation from folded-chain to extended-chain type crystal structure. If the (local) fibre temperature exceeds $T_m^f$ two possibilities are encountered:

a. Drawing at: $T_m^f < T < T_m^2$
   In this case the drawing process becomes ineffective comparable to isothermal drawing in region-2 (drawing of the melt);

b. Drawing at: $T < T_m^f$
   Once solution-spun/cast UHMW-PE has been heated above the melting temperature and re-crystallized, the favourable topology for ultra-drawing is lost almost instantaneously. Consequently ultra-drawing becomes impossible.

In the actual practice of gelspinning via continuous extrusion and multi-stage drawing the operating conditions are chosen so as to optimize between polymer concentration, molecular weight and fibre properties. The drawing temperature $T$ of T-profile is chosen to prevent melting/recrystallization i.e. $T < T_m^f$. In optimizing continuous extrusion/multi-stage drawing of UHMW-PE, both the polymer concentration and $\lambda_{\text{max}}$ can be increased compared to batchwise solution preparation and isothermal drawing, which makes gelspinning attractive in terms of price-performance.

Recently alternative routes to chain-extended polyethylene structures have been published $^{27,28}$ comprising extrusion of disentangled UHMW-PE in the form of single crystals $^{27}$ or drawing of films of nascent polymer $^{28}$. In view of the fast decay of drawability upon heating/re-crystallization as discussed above,
these solvent-free processes seem to be limited to solid state extrusion i.e. below $T_m^1$.

OTHER FLEXIBLE POLYMERS

The invention of the gelspinning process for polyethylene stimulated the utilization of this concept for other flexible polymers.

High-molecular weight polypropylene was investigated in detail by Peguy and Manley $^{29}$. Ultra-drawing of dried PP-gels resulted in oriented structures possessing tenacities of about 1 GPa and corresponding moduli up to ca. 35 GPa. The moduli are close to the theoretical limit ($\sim 40$ GPa) but of course rather low in comparison to PE due to the helical conformation of isotactic PP in the crystalline state.

Interesting results have been obtained for polyvinylalcohol (PVAL). High-molecular-weight PVAL was synthesized ($M \sim 10^3$ kg.mole$^{-1}$) by Allied researchers and spun/drawn. Tenacities up to 2.3 GPa and corresponding moduli of about 70 GPa were reported $^{30}$. However recently Toray $^{31}$ reported similar values for tenacity and moduli based on rather standard type PVAL's with respect to molecular weight, ca. $1-2 \times 10^2$ kg.mole$^{-1}$. This demonstrates nicely the fact that long chains are needed in the case of apolar polymers such as PE and PP. If (inter)chain interactions increase the chain length can be reduced and in particular tenacity values remain at a high level provided that chain-extension is obtained.

In the near future new developments are to be expected in the area of flexible polar polymers. Unfolding of lamellar crystals into chain-extended structures is accomplished for the apolar polymers such as PE and PP but in the case of for example the polyamides specific hydrogen-bonding between chains in the crystals makes the drawing/unfolding process difficult. Consequently no impressive results have been published up to now concerning gelspinning of (high-molecular-weight) polyamides and polyesters but research will continue in view of the intriguing gap between theory and practice, see Tab. 1.
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