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Ultra-drawing of high molecular weight polyethylene cast from solution

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With 2 figures and 1 table

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Introduction

It has been recognized for a long time that the ultimate mechanical properties of polymeric materials depend on the molecular weight and the extension and alignment of the macromolecules. Therefore it seems advantageous to orient high molecular weight polymers by e. g. drawing melt-spun fibers or solid-state extrusion (1–3). These attempts fail, however, under conditions where the molecular extension process is most effective, i. e. at temperatures below the melting point of the polymer (1–3). This is primarily due to the high viscosity of these high molecular weight materials, which causes fracture upon drawing.

Recently, we reported a greatly increased effective drawability of filaments of high molecular weight polyethylene ($\bar{M}_w = 1.5 \times 10^6$) that were obtained from solutions (4–6). For example, poyethylene fibers that were spun from a 2 % w/w solution in decalin could readily be drawn to a draw ratio of 30 at a temperature of 120 °C and at a strain rate of 1 s^{-1}. Under similar drawing conditions melt-crystallized material of the identical polyethylene sample could be elongated only by 5 times (3, 6, 7). The filaments produced by the solution-spinning/drawing technique exhibit excellent mechanical properties, which is reflected by a tensile strength and Young's modulus at room temperature of 3.0 GPa and 90 GPa, respectively.

This communication elaborates on the interesting phenomenon of the increased processability of high molecular weight polyethylene that is obtained from solutions. Some preliminary results will be presented of a comparative study on the drawing behavior of melt-crystallized and solution-cast high polymers.

Experimental

The high molecular weight polyethylene Hostalen GUR with $\bar{M}_n = 2 \times 10^5$ and $\bar{M}_w = 1.5 \times 10^6$ was used in this study. The compacted powder was compression moulded into 0.16 mm sheets at 160 °C. These films were solidified by quenching to room temperature. In addition, films of the

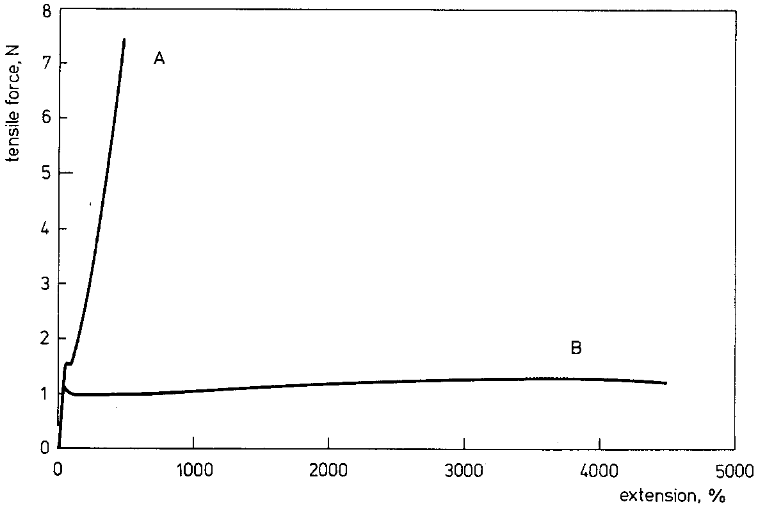

Fig. 1. Load/extension curves recorded at 120 °C for high molecular weight polyethylene. A - melt-crystallized film; B - film cast from a 2 % w/w solution in decalin, subsequently freed from solvent

identical polymer sample were produced by casting from a solution of 2 % w/w of the polyethylene in decalin (decahydronaphthalene, J. T. Baker Chemicals). The polymer solution was prepared at 160 °C under nitrogen, and was stabilized by 0.5 % w/w (based on the polymer) of the antioxidant di-*t*-butyl-*p*-cresol. It was described previously (4,5) that upon quenching such a dilute solution of high molecular weight polyethylene a polymer gel is generated. The solvent was allowed to evaporate from this gel at room temperature leaving a polyethylene film with a thickness of 0.14 mm that contained still 4 % w/w of decalin. This last trace of solvent was removed by extraction with ethanol. The density of the solution cast film was 0.92 g/cm^3, which is somewhat lower than the value of 0.94 g/cm^3 found for the melt-crystallized sample. This reduced density is partially due to a reduced crystallinity (5), but it is primarily a result of some remaining porosity of the solution-cast film.

Dumb-bell shaped specimens of 20 mm gauge length and 2 mm width were cut from the solidified and fully dried polyethylene films.

The drawing behavior of the samples was examined with an Instron tensile testing machine that was equipped with a temperature regulated oven. The oven was maintained at 120 °C ± 1 °C throughout this study. A standard cross-head speed of 100 mm/min was adopted in the hot-drawing experiments. The draw ratio was determined in the usual

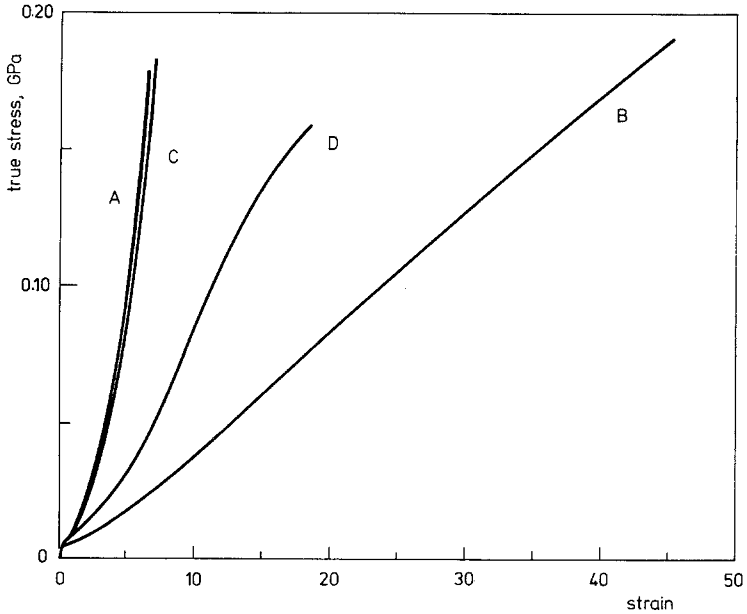

Fig. 2. True-stress/strain curves recorded at 120 °C. A - melt-crystallized film; B - film cast from dilute solution; C - film B stored at 200 °C for 15 min; D - film B annealed at 130 °C for 15 min

way by measuring the distance between ink marks placed onto the specimen 1 mm apart, prior to drawing. Some of the drawn samples were subsequently tested at room temperature. Here the initial specimen length was 50 mm and the testing speed was 5 mm/min.

Results and discussion

Figure 1 shows typical load/extension curves of the melt-crystallized and solution-cast films recorded at 120 °C (curve A and B, resp.).

Curve A of the melt-processed material is characterized by a strong increase of the tensile force with increasing extension. Fracture of the specimen occurred at an elongation of 600 %.

The solution-cast films displayed a rather different hot-drawing behaviour (curve B). Here the drawing process required a relatively low tensile force. The elongation at break was 4 500 %, which exceeded the value for the melt-crystallized specimen by 7.5 times.

The true-stress/strain curves were calculated from these load/extension curves in order to account for the difference in thickness of the two films, and for the decreasing specimen cross-section with increasing elongation. These calculations were performed in the usual way employing the following relations

$$\sigma = \frac{F}{A_0}\,\lambda \qquad [1]$$

$$\lambda = \frac{L}{L_0} = \varepsilon + 1\,. \qquad [2]$$

Here σ denotes the stress, F refers to the tensile force and A_0 is the initial cross-sectional area of the specimen. λ is the draw ratio, L ist the length, L_0 denotes the initial sample length and ε is the strain. Formula [1] assumes a constant volume of the specimen during drawing, which is correct within sufficient accuracy. The true-stress/strain curves that correspond with the load/extension curves in figure 1 are presented in figure 2. It is seen in this figure that the ultradrawn specimen fractured at a true stress of 0.19 GPa, which is but slightly higher than the value of 0.18 GPa, where the melt-crystallized sample failed at 120°C.

The anomalous drawing behavior of the solution-cast film was lost completely upon heating this polyethylene sample for 15 min at 200 °C. The true-stress/strain curve of this melted and recrystallized film is given in figure 2 (curve C). It is shown in this figure that this curve C virtually coincides with the one of melt-crystallized polyethylene (curve A). Also heating the solution-cast film for 15 min at 130 °C seriously affected the stress-strain behavior and the maximum draw ratio attained (see curve D). Previously conducted differential scanning calorimetric measurements on these dried gels of high molecular weight polyethylene showed that about 30 % of the polymer was molten at 130 °C (4,5). The (partial)melting and recrystallization of the solution-cast films was accompanied by a slight change in density. These values were all found in the range from 0.93–0.94 g/cm^3.

It should be noted that the presented true-stress/strain curves were recorded at a constant cross-head speed. Accordingly, the drawing process proceeded at a steadily decreasing strain rate ($\dot{\varepsilon}$). This affects the shape of the true-stress/strain curves, since the drawing stress appeared to decrease with decreasing strain rate. However, the principal features of the difference in hot-drawing behavior of melt-processed and solution-cast high molecular weight polyethylene are not obscured.

It is noteworthy that the present set of true-stress/strain curves show a striking similarity with those recorded for polyethylene samples having varous molecular weights that were crystallized from the melt (e. g. 8), and for rubbers with different amounts of crosslinks (e. g. 9). *Vincent* (8) reported that the rate of strain hardening in polyethylene (i. e. the slope of the stress-strain curve) decreases with decreasing molecular weight. He discussed this phenomenon in terms of a reduced number of entaglements in polyethylene with a low molecular weight, invoking the analogy with the deformation of a rubber with a decreased crosslink density.

In an earlier paper (6) the drastically increased drawability of high molecular weight polyethylene fibers spun from solutions related to melt-crystallized material was qualitatively explained with a favourable intermolecular topology of the macromolecules with a highly reduced number of entanglements in these solutions. It was suggested that, upon quenching such a solution, this partially disentangled structure is fixed by the formation of a polymer gel with crystallites acting as physical crosslinks, provided that the polymer concentration exceeds the overlap concentration. The present observations concerning the hot-drawing behavior of high molecular weight polyethylene that is obtained from solution, and the resemblance with drawing of low molecular weight melt-crystallized polyethylene or rubbers with a low crosslink density, seem to corroborate this view. Melting and recrystallization of the solution-cast film, which gave rise to a rapidly increasing rate of strain hardening, can then be understood in terms of re-entangling of the polymer molecules.

In table 1 the mechanical properties at room temperature are presented of both a melt-processed and a solution-cast film that were drawn 6 times at 120 °C. It is obvious from the data shown in figure 2 that these samples were drawn at a markedly different drawing stress. Table 1 illustrates that the mechanical properties of these drawn polyethylene films were quite similar. This observation indicates that these physical properties were largely determined by the draw ratio, rather than by the drawing stress, as was already noted before by other authors (e. g. 10).

The room temperature tensile strength, Young's modulus and strain at break of a 40 times drawn solution-cast film are also given in table 1. The modulus and strength of, respectively, 108 GPa and 3.0 GPa illustrate the excellent mechanical properties of the solution-cast/drawn polyethylene films. A final remark should be made about the very high draw ratio of 46 currently achieved in hot drawing of the solution-cast film. Previously, we reported that fibers spun from a solution of the same polyethylene sample could be drawn to a draw ratio of 32 (4–6). This lower value was, however, attained at a strain rate of about 1 s^{-1}, whereas in the present study the strain rate just prior to fracture at ε = 45 amounted to only 0.0018 s^{-1}. The influence of the strain rate on the drawing behaviour will be dealt with in more detail in a forthcoming paper.

Table 1. Mechanical properties of high molecular weight polyethylene drawn at 120 °C

Sample	Draw ratio	Drawing stress GPa	Tensile strength GPa	Young's modulus GPa	Strain at break
melt crystallized	6	0.13	0.5	10	0.09
solution cast	6	0.02	0.6	13	0.08
solution cast	40	0.17	3.0	108	0.05

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Summary

Hot drawing of high molecular weight polyethylene ($\bar{M}_w = 1.5 \times 10^6$) was studied. It was found that solution-cast films exhibited a drastically increased drawability in comparison with melt-crystallized material. This phenomenon, which enabled the production of polyethylene structures with a Young's modulus of 108 GPa and a strength of 3.0 GPa, is discussed in terms of a reduced number of entanglements in solution-crystallized material related to melt-crystallized films.

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