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Spinning of High Molecular Weight Polyethylene Solution and Subsequent Drawing in a Temperature Gradient

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SUMMARY

The spinning and drawing of high molecular weight polyethylene solution forming ultra-high strength fibres has been studied and occurrances on the molecular level are discussed. The fibre properties were found to be strongly influenced by the drawing stress and the temperature conditions.

INTRODUCTION

Melts and concentrated solutions of flexible polymer molecules are known to exhibit a network-like deformation behaviour originating in the presence of numerous molecular entanglements and intertwinings (BUECHE, 1952; FERRY, 1961; GRAESSLEY, 1974), which represent centres of friction (CHÖMPFF,DUISER, 1966) for molecular motion. Though some of these may be removed by slippage of molecules past each other during deformation, a considerable number will be trapped during fibrous crystallization (PENNINGS, 1979). Entanglements, intertwinings, chain ends, loops and other defects (PREDECKI, STATTON, 1967) are responsible for the lack of tensile strength and modulus in oriented polymers (PENNINGS, 1979). Accordingly, minimizing the number of these defects, i.e. by using high molecular weight polymers and polymer solutions of low concentrations, should result in fibres of high strength and modulus. Zwijnenburg and Pennings (ZWIJNENBURG, PENNINGS, 1976) have already taken advantage of this possibility in their work on the surface growth of polyethylene fibres, where they used polyethylene of high molecular weight (M_w = 1.5 x 10^6) in solution having a concentration of about 0.5% by weight.

In the surface growth technique, the long chain molecules are aligned close to the equilibrium dissolution temperature by stretching the entangled network which is anchored at both the rotor surface and the seed fibre. Here, a certain minimum number of entanglements appear to be necessary for the stretching to occur, since these entanglements in the state of supercooling may be the nuclei for small crystallites

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which then support strength to the network during drawing. It is of interest to note that (CAPACCIO, WARD, 1975) have already considered the high molecular weight polymer fractions that form an entanglement network as playing an important role in the drawing behaviour of fibres. Following the surface growth mechanism, it might be envisaged that a simple drawing process of an entangled high molecular weight polymer solution, under similar conditions, would yield fibres having comparable properties. Studies on the spinning and drawing of high molecular weight polymer solutions have already been carried out earlier by (FRENKEL et al., 1964), (ZWICK, 1967) and (SMITH et al.).

It is shown in the present study that the spinning and drawing of high molecular weight linear polyethylene solutions, at high temperatures, results in the formation of fibres with tensile properties similar to those of the surface growth fibres. From the experiments, it appears that the tensile strength is mainly related to the stress applied during the drawing process and the temperature conditions.

EXPERIMENTAL

The linear polyethylene used in the present study was Hi-fax having a weight average molecular weight of about 4×10^6 kg/kmole. The polyethylene was dissolved in dodecane after addition of antioxidant at a concentration of 5% by weight under constant and slow stirring over 48 hours at a temperature of 150°C. Spinning of the solution (POSTHUMA DE BOER, PENNINGS, 1976) was performed through a conical capillary in order for the fibre to orient sufficiently and thus be able to withstand the applied drawing stresses. The fibre to be drawn had a polymer concentration between 10 and 15% by weight. Drawing experiments were carried out in a double-walled glass cylinder through which hot silicon oil was streaming at a slow rate, therefore establishing a change in temperature from 100 to 148°C over a length of 1 m. By increasing the flow rate, a nearly constant temperature over the tube length could also be achieved. The velocity of the fibre entering the tube was 2.65 cm/min. Stress on the fibre during drawing was applied by means of a free-hanging wheel positioned before the wind-up.

RESULTS AND DISCUSSION

The necessity of applying a temperature gradient was found from preliminary experiments which indicated that fibre breakage occurred at the entrance of the drawing tube when a high temperature, that was constant over the length, was applied. By lowering the temperature at the entrance, failure could be avoided. This behaviour might be related to the fact that the polymer concentration of the fibre increases from 10% by weight to 100% due to evaporation of the solvent. Furthermore,

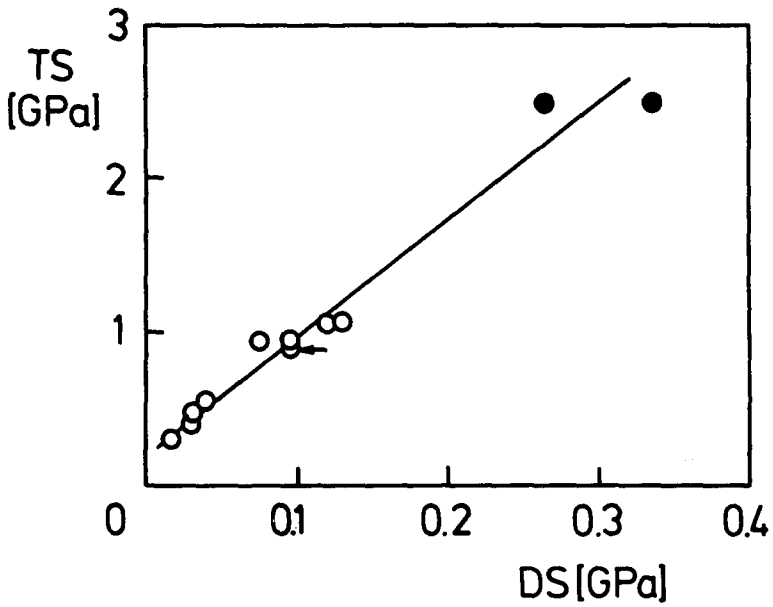

Figure 1: The tensile strength at break, TS, as a function of the drawing stress, DS, for fibres drawn from entangled polyethylene solutions. The open circles represent the tensile strengths of fibres drawn in the temperature gradient, while the full circles indicate the results from a second drawing experiment, at constant temperature in the drawing tube, on a previously drawn fibre (arrow in the figure).

these experiments showed that in order to obtain a high strength, an optimum temperature at the exit of the tube of 148°C, which is nearly 3°C above the equilibrium melting temperature, should be applied.

In all experiments the drawing stress was observed to be the most important parameter influencing the tensile strength of the drawn fibres. Figure 1 shows the dependence of the tensile strength at break on the drawing stress. Here the drawing stress is defined as the applied drawing force divided by the cross-sectional area (calculated from the fibre weight and length by employing a density of 1000 kg/m^3) of the drawn fibre.

The experiments carried out in the temperature gradient are represented by the open circles in the figure. In the second drawing process on a previously drawn fibre (marked by the arrow in Figure 1), without a temperature gradient but at a slightly higher temperature (153°C), fibres with markedly higher tensile strengths were obtained (full circles). The draw ratio, given by the ratio of the speeds at the exit and the entrance of the drawing tube, for the strongest fibre in Figure 1 was about 38. It appears from the present data that the tensile strength is almost linearly related to the drawing stress. This dependence on the stress might lead to the following interpretation of the drawing mechanism. The applied drawing stress induces, in poor crystals, melting and reorientation of molecules, followed by crystallization and formation of fibrous crystals of higher perfection; while crystals of still higher perfection do not melt and, therefore, supply strength to the fibre during drawing. It should be noted that a decrease in the melting temperature of poor crystals may take place as a result of an increase in free energy of the crystal, due to the application of stress. In addition to melting of poor crystals, the stress also increases the rate of creep, and thus, the rate of migration of defects (PREDECKI, STATTON, 1967; KALB, PENNINGS, in print), leading also to the formation of crystals of high perfection. In the drawing process, low molecular weight fractions (BARHAM, KELLER, 1976; CAPACCIO et al., 1976; WARNER, 1978) and the solvent may act as plasticizers, and accordingly, raise the drawability of the fibre.

Figure 2 shows the equatorial reflections of an X-ray diffraction pattern produced from a single fibre, with a strength of 2.5 GPa, whose molecular orientation appears to be very high.

In an effort to elucidate the influence of the molecular weight on the fibre properties, drawing experiments were carried out under the same conditions, with fibres from which the low molecular weight polymer was extracted (POSTHUMA DE BOER, PENNINGS, 1976). A comparison of the fibre strength with that of the unextracted fibres indicated no significant increase in

strength.

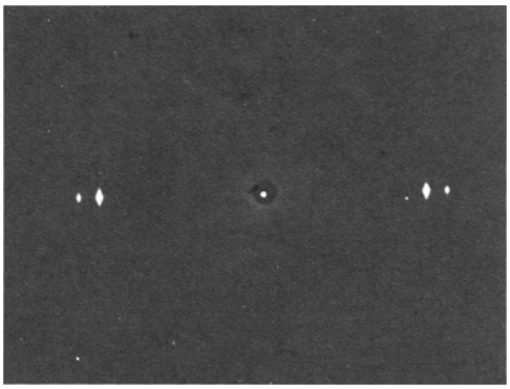

Figure 2: Equatorial X-ray reflections produced by a single fibre having a tensile strength of 2.5 GPa.

It may therefore be concluded, for the present case, that the number of entanglements present has a more pronounced influence on the tensile strength than the number of chain ends.

Finally, it should be mentioned that fibres with tensile properties exceeding those given above were obtained by spinning and subsequent drawing the precipitate of a 1% solution in decaline. The fibres were drawn only once in the temperature gradient, starting with a concentration of about 10%. At a drawing stress of 0.68 GPa, the tensile strength amounted to 3.5 GPa. This result seems to underline the importance of the polymer concentration and probably also the nature of the solvent. The nature of the solvent has probably an effect on the number of intra-molecular entanglements while the concentration mainly determines the number of inter-molecular entanglements. Furthermore, the viscosity of the solvent might also contribute to the mobility of molecules and might therefore affect the rate of drawing. Further studies on this subject are being carried out.

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