polymer communications

Hot drawing of porous high molecular weight polyethylene

B. Kalb and A. J. Pennings
Department of Polymer Chemistry, State University, Groningen, Groningen, The Netherlands
(Received 20 June 1979; revised 25 September 1979)

It has been shown by Capaccio, Crompton and Ward[1] that high molecular weight linear polyethylene can be drawn to form high modulus fibres. However, the drawing of such fibres cannot proceed to high draw ratios and is impeded by a high number of failures due to fracturing. On the other hand, small and intermediate molecular weight polyethylene can easily be drawn to high draw ratios[1]. It appears that the drawability of polymer fibres is influenced by the mobility of the polymer molecules, which is determined by various parameters, as expressed by the simplified equation for non-recoverable creep[2]:

$$\dot{\epsilon} = A\exp[-(U_a - \sigma v)/kT]$$

where $\dot{\epsilon}$ is the rate of creep, and U_a, σ and v represent the activation energy for transport, the tensile stress, and the activation volume respectively. The activation volume is the free volume necessary in order that unfolding of molecules, migration of crystal defects, and creep of molecules to allow local stress relaxation can occur. k and T are the Boltzmann constant and the absolute temperature respectively, and A is a constant. Both stress and activation volume decrease the energy barrier for transport and, therefore, increase the rate of creep. It was found[2] that the activation volume for high molecular weight polyethylene is considerably smaller than for that of low molecular weight. Furthermore, there is evidence that non-recoverable creep does not take place below a critical value of $\sigma v/kT$ for high molecular weight polyethylenes, which is a finding of great practical importance. These observations imply that at low values of v, the stress must be high in order for creep to occur. Accordingly, since at large draw ratios the drawing stress is principally high, and for a high molecular weight sample becomes still higher due to the low v, this effect during drawing should lead to a greater probability of fracture for high molecular weight materials than for those of low molecular weight, as has actually been observed in experiments[1].

According to the discussion above, it may follow that an increase in the free volume, in the form of a high microporosity of the fibre to be drawn, will yield an improved drawability of high molecular weight polymers. The purpose of the present note is to show that the drawing process is indeed influenced by the microporosity of the fibres of ultra-high tensile properties similar to surface growth[3,4] and solution drawn fibres[5] can be formed.

The linear polyethylene used in the present study was Hi-Fax with a weight average molecular weight of about 4×10^6 kg kmol^{-1}. The porous fibre was produced by spinning a 5% (by wt) polyethylene solution in paraffin oil through a conical die, extracting the paraffin oil in *n*-hexane, and drying the fibre under vacuum. The porosity, calculated from the weight and the volume of the fibre by employing a density for polyethylene of 950 kg m^{-3}, amounted to about 0.55 cm^3 free volume cm^{-3} porous fibre. During spinning, the fibre obtained a slight orientation that was high enough to withstand the applied drawing stresses. The drawing temperature conditions were maintained by a double-walled glass cylinder, about 1 m in length, through which silicon oil was allowed to flow at a slow rate so that a temperature gradient between the ends of the tube could be established. The lower temperature at the entrance and the higher temperature at the exit of the tube were 100°C and 148°C respectively. The need for the temperature gradient was derived from preliminary experiments without a temperature gradient which showed that the drawing, and therefore the change in cross-section, occurred at a narrow region of the fibre which was positioned exactly there where the temperature increased suddenly from room temperature to the drawing temperature. A slow change in the fibre cross-section during drawing was thought to be advantageous for

Table 1 The draw ratio, cross-sectional area, and the tensile properties of the porous fibres drawn at various drawing stresses. Note that the actual draw ratio is slightly higher than that given in the table (see text). The cross-sectional area was determined from the weight and the length of the fibre by employing a density of 1000 kg m^{-3}

Sample no.	Drawing stress 10^7 Pa	Draw ratio	Cross sectional area 10^{-8} m^2	Tensile strength GPa	Elongation at break %	Initial modulus GPa
1	1.65	2.8	6.10	0.37	9.4	11.8
2	4.7	6.0	3.18	0.65	7.6	20.6
3	16.4	12.6	1.22	1.81	6.7	41.2
4	40.3	16.2	0.55	3.0	6.4	106.0

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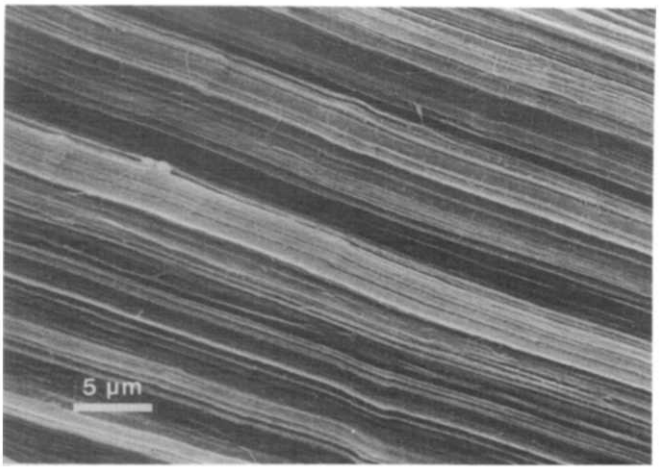

Figure 1 Scanning electron micrograph of the fracture surface of fibre no 4

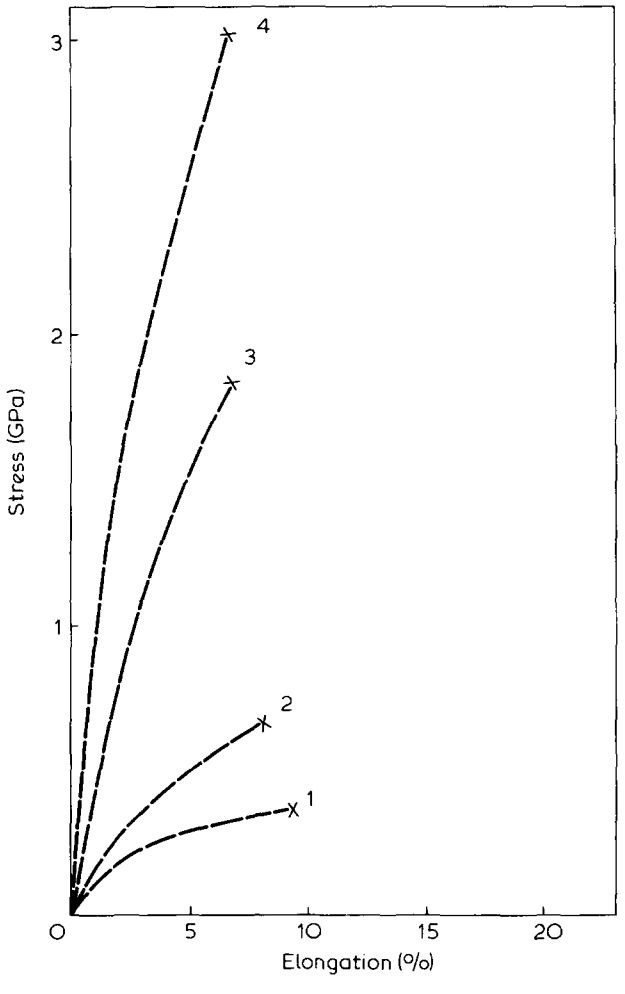

Figure 2 Stress/strain curves of the samples given in *Table 1*, measured at a cross-head speed of 12 mm min^{-1} and an original length of the fibre of 25 mm

the rearrangement and creep process of long molecules. Moreover, it appeared from these preliminary experiments that fibres drawn in the temperature gradient had higher tensile properties. The speed of the porous fibre at the entrance of the drawing tube was kept constant at 2.65 cm min^{-1}. The fibre leaving the tube was led over a free-hanging wheel which served for the application of the draw-stress.

During drawing, the drawing stress was increased step by step up to a maximum stress above which the fibre fractured. *Table 1* contains a summary of the experimental results obtained at different drawing stresses. As can be seen, the strength and modulus of the fibres increase with the drawing stress. At the maximum stress of about 0.4 GPa and a draw ratio of 16.2, the fibre achieved remarkably high tensile properties of 3.0 GPa in strength and 106 GPa in initial modulus. The draw ratio referred to in this study is given by the ratio of the speeds at the exit and the entrance of the drawing tube. Due to the slight orientation of the undrawn fibre, the actual draw ratio is higher than that observed experimentally. The elongations at break are higher than for the fibres produced by the surface growth technique[3,4].

Figure 1 is a scanning electron micrograph of fibre no. 4 which shows that the molecular orientation is apparently very high.

The stress/strain curves of the samples given in *Table 1* are presented in *Figure 2* where it can be seen also that the tensile properties increase significantly for samples with a higher drawing stress.

It has been shown in the present study that fibres of extremely high tensile properties can be formed by drawing of porous high molecular weight polyethylene. The presence of pores apparently increases the molecular mobility necessary to obtain complete alignment of the polymer molecules and allow the migration of crystal defects towards the amorphous regions of the fibre. Similarly, the free volume between molecules and crystallites seemed to have lowered the energy barrier for the transport of polymer molecules, as already predicted by the creep equation. Whether the high surface free energy of a porous fibre plays an important role in the drawing process has to be further investigated.

ACKNOWLEDGEMENT

The assistance of T. J. Versélewel de Witt Hamer in the experimental work is gratefully acknowledged.

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