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Shrinkage as a measure of the deformation efficiency of ultra-oriented high density polyethylene

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A simple test is described that allows the evaluation of the molecular extension in solid state extruded high density polyethylene at maximum extrusion draw ratio 36. The samples, which were prepared by shaving the extrudates to films of average thickness 0.4 mm, were melted very rapidly and shrunk at 160° C. Experimental evidence shows that at high heating rates (800° C min^{-1}) all the molecular extension is recovered elastically. The variation of shrinkage with molecular weight indicates a difference in the molecular extension produced during the extrusion, and a simple relationship between molecular draw ratio and modulus is considered.

1. Introduction

In recent years there has been great interest in polymers with a high degree of chain elongation and orientation because of their high modulus and strength, relative to weight. Numerous methods [1] are used to produce high chain orientation such as wet and dry spinning, drawing and extrusion. In all cases, the efficiency of inducing and maintaining chain elongation is crucial in producing high modulus products. The deformation of high density polyethylene by the solid state extrusion technique has produced samples with tensile modulus up to 70 GPa [2]. In this report we wish to discuss the results of a simple shrinkage test, performed at fast heating rates above the melting point as a measure of chain elongation.

Drawn polymers when heated close to the melting point show shrinkage of 50% or more. Peterlin [3] used this observation as key evidence in his amorphous tie molecule model of drawn fibre structures. Pennings and van der Mark [4], and Grubbs and Keller [5] have studied the shrinkage of solution grown shisk-kebab structures on melting and super-heating of the extended chain backbone. They used slow heating rate and studied melting points, the loss of bi-refringence and the effect of temperature cycling. They noted a strong dependence of shrinkage on sample thickness arising from non-uniform heating of the sample. When molten and solid polymers coexist the solid regions act as a rigid support preventing shrinkage.

The dimensional changes of extruded rods was discussed in detail by Capiati and Porter [6]. They found a reversible negative expansion coefficient in the chain direction below 100° C; this is evidence for a high degree of chain orientation. Imada *et al.* [7] observed irreversible shrinkage above the extrusion temperature (110° C) in extruded HDPE rods in contrast to drawn HDPE that shows shrinkage at 20 to 30° C below the drawing temperature (80° C).

Barham and Keller [8] have compared the shrinkage of fibrous polyethylene prepared by several different methods and analysed the results in terms of the morphology differences. They suggest that the relative absence of shrinkage below the melting point indicates that the elongated chains or "tie molecules" [3] are held in crystalline regions in the solid state extrudates.

2. Experimental

2.1. Extrusion

HDPE extrudates were prepared by the techniques used previously in this laboratory [2, 9]. Melt

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TABLE I Shrinkage and modulus data for a variety of extrudates

					Tensile Modulus (GPa)
Alathon 7050 rod	120	12	44	5.3	10
Alathon 7050 rod	120	24	46	11.0	27
Alathon 7050 rod	120	36	46	16.5	40
Alathon 7050 p–p*	110	36	51	18.4	40
Alathon 7050 p–p	95	36	56	20.2	48
Alathon 7050 p–p	90	36	59	21.2	52
Alathon 7050 p–p	85	36	61	21.9	55
Marlex 6003 s–b†	120	24	76	18.2	46
Marlex 6003 s–b	110	12	85	10.2	18

* p–p, push–pull processing.
† s–b, split billet processing.

crystallized billets were prepared by compression moulding under vacuum. They were extruded in an Instron capillary rheometer with diameter 0.95 cm through a brass conical die with a 20° entrance angle. The extrusion temperature (T_{ext}) and draw ratio (EDR) conditions are summarized in Table I. The EDR was defined by the ratio of the inlet to the outlet cross-sectional areas of the die. In this study two linear high density polyethylenes were used for comparisons. The DuPont Alathon 7050, a low molecular weight resin ($M_w = 59\,000$) subsequently referred to as low MWPE and the Phillips Marlex 6003, a high molecular weight resin ($M_w = 250\,000$) referred to as high MWPE.

Three different methods of extrusion were used: (1) Conventional solid state extrusion, in which a preformed cylindrical billet was extruded into a oriented rod. (2) The preformed billet was split longitudinally prior to extrusion and the two halves were extruded together, i.e. the split billet process [10]. (3) A load was attached to the emerging split billet extrudate to increase the extrusion rate, i.e. the push–pull extrusion process [10]. Previous work in this laboratory has shown that the properties of the low MWPE extrudates prepared under identical conditions are independent of whether the conventional split billet or push–pull extrusion process were used. In contrast, for the high MWPE, the split billet extrudate has a much higher modulus than the rod extrudate. Recent work suggests that the modulus* of the split billet extruded sample truly reflects the extent of chain elongation and the morphology of the extrudate, whereas the modulus of the rod extrudate is reduced because of defects that are generated as the material emerges from the die. (This problem is discussed in great detail in [12].) Therefore, only the split billet extrudate of high MWPE is considered in this report.

2.2. Shrinkage

Samples for the shrinkage test were obtained by shaving the extruded rods longitudinally into films of average thickness 0.4 mm. The films, 1 cm long, were floated in a glycerol bath (density 1.26 g cm^{-3}) to avoid adhesion between the polymer and any rigid surface. A microscope hot state was used for the heating rate studies. For the most rapid heating rate, the film samples were placed in a glycerol bath that was preheated to 160° C. As soon as the film was molten it became transparent and shrunk. The molten film still had structural rigidity, and was removed from the bath to recrystallize. The change in dimensions could be easily and precisely measured with a micrometer. The complete experiment was repeated 5 times; shrinkage results are quoted to ± 3% absolute.

2.3. Tensile modulus measurements

The modulus measurements of the extruded rods, prior to their use in the shrinkage tests, were performed in tension on an Instron TTM tensile tester. The modulus was determined from the tangent to the stress–strain curve at 0.1% strain. The strain was measured using an extensometer. The strain rate was 3×10^{-5} sec^{-1}.

3. Results and discussion

Fig. 1 compares samples before and after shrinkage at 160° C. It shows that coherent films recover after melting and recrystallization, and that

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* Tensile or Young's modulus.

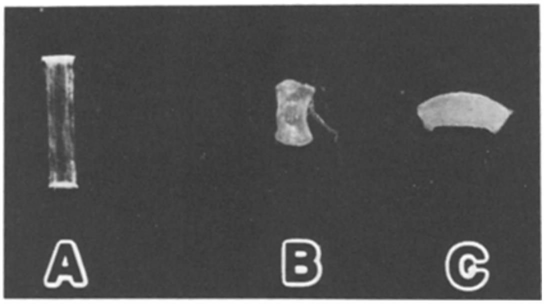

Figure 1 A comparison of samples of low and high MWPE before and after shrinkage: (A) sample before shrinkage, (B) low MWPE after shrinkage, (C) high MWPE after shrinkage.

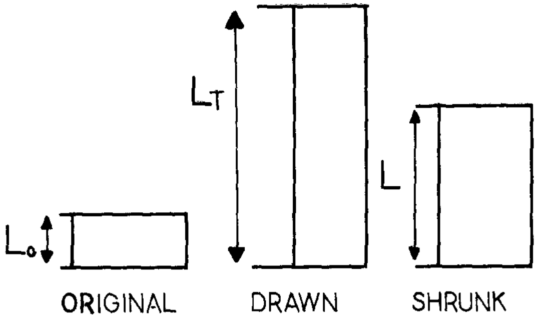

Figure 2 Schematic diagram of the changes in sample length on deformation and shrinkage.

shrinkage varies with polymer molecular weight. Fig. 2 shows a schematic diagram of the changes in dimension during extrusion and shrinkage. Shrinkage is defined as the change in length on melting.

$$\%\ \text{Shrinkage}\ S = \left(\frac{L_\text{T} - L}{L_\text{T}}\right) \times 100$$

where L_T is the length of the sample after deformation and L the shrunk length. The original length prior to extrusion may be calculated from the imposed draw ratio. If all the deformation is recovered, $L = L_0$, the length before deformation. Therefore % recovery R is given by

$$R = \left(\frac{L_\text{T} - L}{L_\text{T} - L_0}\right) \times 100$$

This assumes that no relaxation of orientation occurred in the extruded film sample prior to melting and that there was no residual orientation in the shrunk sample after melting and recrystallization. Either of these effects would lead to even higher values. Their magnitudes are unknown but are assumed to be small.

Shrinkage was also found to depend on film thickness. A low MWPE rod, diameter 1.98 mm extruded at 120° C to EDR 24, shrank by 36% on melting at 160° C; a film cut from an identical extrudate 0.6 mm thick shrank by 43%, and films between 0.5 and 0.3 mm shrank by 50%, independent of thickness. Films longer than 1 cm and less than 0.2 mm thick tended to curl, presumably because the molten film did not have sufficient rigidity to oppose surface tension. In all subsequent tests film samples used were ~ 0.4 mm thick and 1 cm long and the energy required to oppose the surface energy on the sample is ignored.

Fig. 3 shows the effect of heating rate on the recovery of the two different molecular weight polyethylene extrudates. The thin films melted in less than 15 sec when placed in the glycerol bath at 160° C, i.e. at an effective heating rate of about 800° C min^{-1}. The recovery at high heating rates varied with molecular weight. Also, the recovery of the high MWPE extrudate dropped slightly at low heating rates, whereas the low MWPE extrudate showed a relatively sharp discontinuity at a heating rate of 20° C min^{-1}.

To understand this observation, the mechanism of molecular recovery and chain entanglement must be considered. The properties of amorphous polymers above T_g are dominated by molecular entanglements forming a network structure [11]. In the same way, when oriented polyethylene is

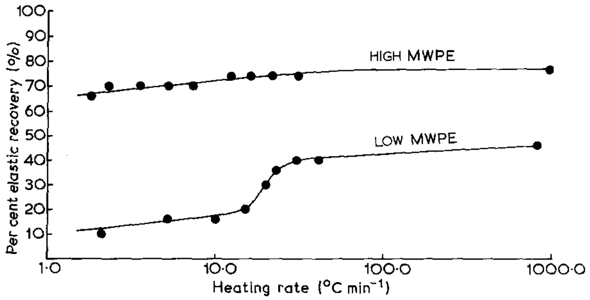

Figure 3 The effect of heating rate on the elastic recovery of high MWPE and low MWPE extruded at 120° C and to EDR = 24.

rapidly melted the chains return to a random coil and cause shrinkage of the sample if there is an entangled chain network. However, there is a limited time for which a molecular entanglement forms a structurally significant cross-link [11], Thus the drop in recovery at low heating rates for the low MWPE extrudate results from the loss of the network structure, and consequently molecular extension is lost by a chain slip process. The number and rigidity of entanglements will be greater in the high MWPE extrudate, so elastic recovery is observed over the full heating rate range. This leads to the important conclusion that for both molecular weights the recovery measured at the highest heating rate probably corresponds to the recovery of all the molecular elongation introduced in extrusion, and therefore it is a measure the molecular extension.

Since the recovery at the highest rate is dependent on molecular weight, the molecular extension introduced during extrusion is dependent on molecular weight and hence on molecular entanglement. Recovery was measured for a wide variety of samples. From the extrusion draw ratio and the percentage recovery, the actual molecular deformation or molecular draw ratio can be calculated.

$$\text{Molecular draw ratio} = \frac{L}{L_0} = \left(\frac{L_\text{T}}{L_0}\right) \times \frac{R}{100}$$

$$= \text{EDR} \times \frac{R}{100}$$

Fig. 4 shows that for a given EDR a wide range of moduli can be obtained. If the same data are plotted against molecular draw ratio (Fig. 5) the points fit on a single straight line within experimental error. This suggests that modulus is solely a function of molecular draw ratio. The effect of varying extrusion conditions and molecular weight is to change the efficiency of deformation, i.e. the ratio of bulk deformation to molecular deformation. This result also suggests that comparisons of other parameters such as thermal properties should be made on the basis of molecular draw ratio. The effect of molecular weight on extrudate properties is discussed in great detail in [12].

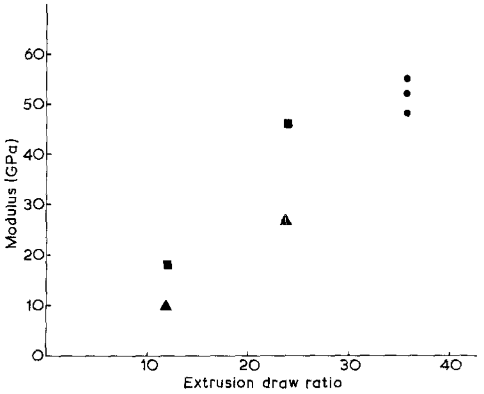

Figure 4 Variation of modulus with EDR for a series of extrudates: ▲ low MWPE rod, $T_{\text{ext}} = 120°\text{C}$, varying EDR; • low MWPE split billet, EDR = 36, varying T_{ext}; ■ high MWPE split billet, varying EDR and T_{ext}.

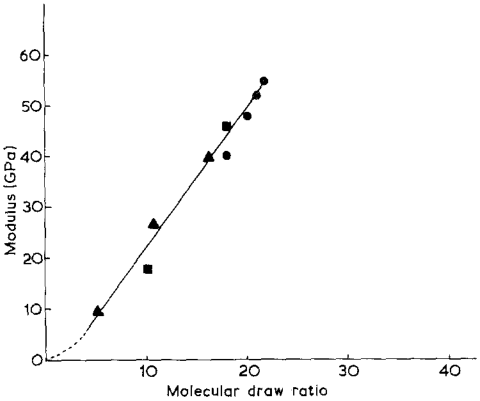

Figure 5 Variation of modulus with molecular drawn ratio, key to symbols as for Fig. 4.

This shrinkage test has also been used as a measure of molecular extension in split billet and rod extrudates [12], and in powdered ultra-high molecular weight polyethylene extrudates [13].

4. Conclusions

(1) Under carefully controlled conditons, notably thin samples and fast heating rates, the shrinkage of oriented HDPE on melting gives a quantitative measure of molecular extension.

(2) Molecular entanglement is found to be significant in both extrusion and shrinkage.

(3) Modulus is shown to be a single linear function of molecular draw ratio.

(4) Changes in extrusion conditions are shown to affect the efficiency of deformation and hence tensile modulus.

(5) Efficiency is independent of extrusion draw ratio at given extrusion temperature and polymer molecular weight.

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