

Morphological changes in pressure annealed polyethylene

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Polyethylene samples have been annealed under high pressures in order to transform the morphology and thereby make specimens, which on subsequent orientation by hydrostatic extrusion, produce high-modulus materials for comparatively low deformation ratios. The pre-extrusion morphology, as revealed by permanganic etching followed by transmission electron microscopy, is shown to be highly sensitive to the annealing conditions, especially in the vicinity of the orthorhombic/hexagonal phase boundary. The morphological changes have also been studied by gel permeation chromatography of nitrated samples and by differential scanning calorimetry. The moduli of samples, extruded to a standard extrusion ratio of 7, reflect differences in the morphology of the starting material. It is shown that the highest modulus is not obtained by annealing totally within the hexagonal phase but rather in the changeover region between it and the orthorhombic phase. Although the lamellar size can be dramatically increased by annealing within the hexagonal phase, this development occurs at the expense of reducing the integrity of the molecular network so that for high lamellar size the modulus falls and the samples become increasingly incoherent.

1. Introduction

A notable feature of polyethylene is the appearance, at pressures typically above 350 MPa, of a stable hexagonal phase between the normal orthorhombic phase and the melt [1,2]. This hexagonal or intermediate phase provides the opportunity to alter the morphology of polyethylene dramatically. Permanent changes can be induced by the process of anabaric annealing, in which a specimen is heated under high pressure beyond the orthorhombic/hexagonal boundary. A large increase in lamellar thickness occurs once orthorhombic crystals change to the hexagonal form [3], and this transformed morphology remains intact on return to the orthorhombic form. It was recognized [4] that alignment of the large lamellae produced in this way might lead to significant improvements in mechanical properties. Sahari *et al.* [5] and Powell *et al.* [6] achieved this using solid-state extrusion to orient anabarically annealed polyethylene. In the more detailed investigations of Powell *et al.* [6] it was also noted that the annealing conditions were critical to the success of the process.

This critical dependence on the annealing conditions, and hence the morphology, is highlighted by the

work of other authors [7,8] who were unable to achieve the same degree of success. It is, therefore, of interest to characterize the morphology most amenable to the development of modulus in subsequent deformation, as well as to identify the particular annealing conditions which produce this optimum morphology. The relation between them, however, is not expected to be unique but will probably depend on other factors such as the grade of material and the initial morphology because the position of the phase boundary on the pressure/temperature diagram (for thick crystals) is sensitive to molecular weight [9,10]; in addition, the actual phase boundary depends on lamellar thickness [11].

This paper is one of a series looking at the effects of high-pressure annealing and subsequent extrusion on several grades of polyethylene. Here attention concentrates on the morphological changes and associated mechanical properties, produced by different annealing conditions, in just one of these grades, a medium molecular weight polyethylene. Several techniques are used to monitor the development of crystallite size in unoriented samples and to relate this to changes in the mechanical behaviour of subsequently oriented

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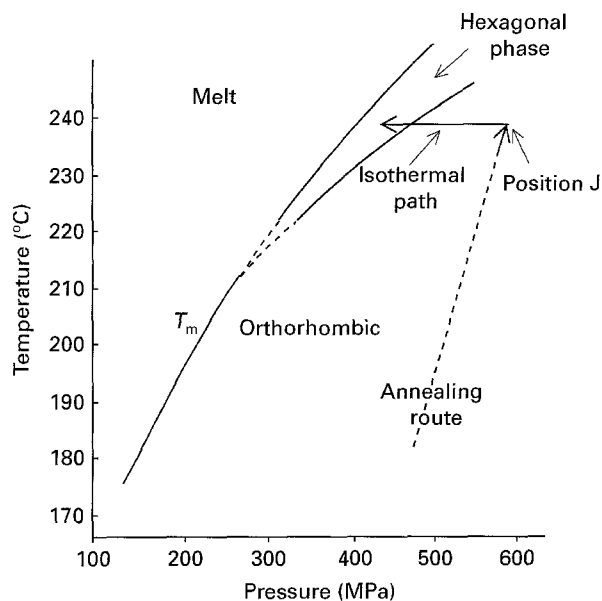


Figure 1 The path of high-pressure annealing in relation to the schematic phase diagram of polyethylene.

samples. As is shown elsewhere [12], changes in the structure of the network, produced during anabarc annealing, are of fundamental importance. Essentially there is a need to balance two conflicting requirements, namely the retention of an adequate molecular network to orient the crystallites effectively, and the changes in morphology which produce large lamellae ultimately at the expense of the integrity of the network.

2. Experimental procedure

The material investigated here is a homopolymer grade of linear polyethylene (HD6007EA supplied by B.P. Chemicals Ltd in pellet form) with number and weight average molecular weights of 25 500 and 135 000 daltons, respectively. The feedstock, prepared from the pellets by melt extrusion at 200 °C into an aluminium mould followed by slow cooling, was machined into billets of 7.5 mm diameter and length of about 130 mm; these billets of the starting material were then subjected to anabarc annealing.

Samples were annealed at various positions in the phase diagram (Fig. 1), straddling the orthorhombic to hexagonal phase boundary. The annealing apparatus, described in detail elsewhere [6], consisted of a thick-walled cylindrical vessel surrounded by heater bands. One end of the central shaft was attached to a closed pressure-monitoring system and pressures were generated by driving a piston into the open end of the shaft using a tensile testing machine. All procedures started from a common basis, applying pressure to a level of about 300 MPa before switching on the heaters. In this way all samples could be taken first to a reference point labelled J in Fig. 1, at a pressure of 585 MPa and a temperature of 234 °C. Fine adjustments to the crosshead position allowed the reference pressure to be maintained as the sample approached thermal equilibrium. From this point the phase boundary could be crossed by reducing the pressure

and following the isothermal path illustrated in Fig. 1. Alternatively, increasing the temperature under constant pressure would also take the sample across the phase boundary, along an isobaric path. In this work the isothermal path was used because it allowed greater flexibility and more accurate control.

At this point it is convenient to identify the "standard annealing conditions" (pressure 500 MPa, temperature 234 °C and a time of 60 min), around which the investigation concentrated. Three sets of samples, in each of which one of the annealing parameters was varied systematically about its standard value, were prepared. (For each set the other two parameters were fixed at their standard values.) After annealing, the sample was returned to the reference position, J, and the heaters switched off. The pressure was maintained at this level for 10 min and then allowed to fall naturally as the sample cooled to ambient conditions when it was removed for subsequent hydrostatic extrusion. Extrusion was performed at 100 °C through a conical die of semi angle 15° and exit diameter 2.5 mm at a constant rate of 5 mm min⁻¹. A nominal deformation ratio of 7 was used throughout.

The melting behaviour of the isotropic annealed samples was examined on a Perkin-Elmer differential scanning calorimeter (DSC 7) using a heating rate of 10 K min⁻¹. Transmission electron microscopy (TEM) was performed on permanganically etched specimens [13] to obtain lamellar thicknesses and morphological characterization. Nitric acid etching followed by gel permeation chromatography (GPC) was used to investigate in further detail the lamellar thickness produced by anabarc annealing [14].

Static three-point bend tests were performed on samples of aspect ratio greater than 40 to determine the 10 s isochronal bending modulus of the sample at 20 ± 3 °C. These measurements were only made on the extruded samples.

3. Results

3.1. Differential scanning calorimetry

The DSC results, given in Table I, show that the morphology of the isotropic samples produced by anabarc annealing is clearly sensitive to the annealing conditions. Results for set 1 plotted in Fig. 2 show that as the annealing pressure is reduced from the reference value of 585 MPa to a value of 450 MPa under otherwise standard annealing conditions, there are considerable changes in both the peak melting point and crystallinity. Even at the reference point, J, the melting point and crystallinity are clearly higher than those of conventionally melt-processed material (e.g. sample R in Table I). At 450 MPa, the crystallinity is above 95% and the melting point is close to that predicted for an infinitely thick crystal [15, 16]. The most pronounced changes, however, occur in a limited pressure range between about 540 and 480 MPa.

DSC traces also reveal evidence of more complex changes. This is especially true at low annealing pressures, i.e. below 500 MPa, when a second smaller endotherm, L, appears at temperatures around 125 °C

TABLE I Specimens and their properties

Set	Name	Pressure (MPa)	Temp (°C)	Time (min)	Melting point (°C)	Crystallinity (%)	Morphology ^a	Lamellar size by TEM (nm)	Stem length (nm) by nitric acid treatment/GPC			Modulus E (GPa)
									Peak	A _n	A _w	
1	A	450	234	60	142.7	95.8	E	154	177	690	1780	
	B	480	234	60	141.2	93.3	E	125	169	65	172	33.7
	C	500	234	60	140.2	87.7	T	59	76	43	85	33.4
	D	515	234	60	139.4	86.7	T	61	79	46	96	30.3
	E	545	234	60	135.5	78.8	F	49	64	35	75	14.8
	J	585	234	60	134.4	71.8	F	—	45	30	58	12.1
2	—	500	232	60	137.3	76						24.0
	—	500	234	60	140.2	87.7						33.4
	—	500	236	60	140.4	87.4						28.0
	—	500	238	60	140.6	87.4						28.3
3	F	500	234	5	137.1	79.5	T	52	55	34	69	28.0
	G	500	234	15	138.9	84.1	T	83	123	59	140	34.6
	C	500	234	60	140.2	87.7	T	59	76	43	85	33.4
	H	500	234	180	139.7	87.6	T	44	60	38	80	31.7
4	Y	180	180	60	136.2	60.1	F					
	Z	200	180	60	135.9	60.1	F					
5	R	no pressure treatment			133.0	60.0	F		17	14	28	

^a Morphologies by TEM: F = folded, T = transitional, E = extended.

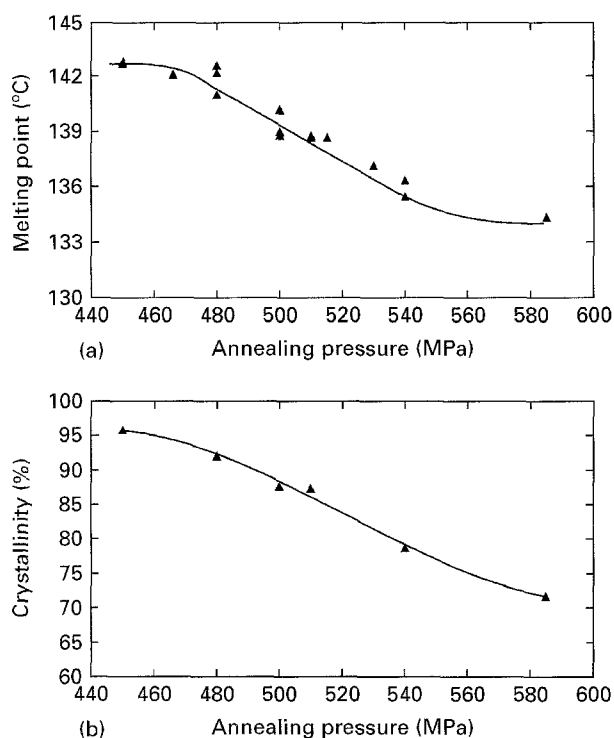


Figure 2 Variation in crystalline morphology: (a) melting point, (b) crystallinity, as a function of annealing pressure. All samples annealed at 234°C and the stated pressure for 1 h.

and a large shoulder, S, develops on the low-temperature side of the main melting peak (Fig. 3). Both features become more prominent as the annealing pressure is reduced.

Results for set 2 in Table I also show that the annealing temperature has a considerable influence on the morphology. In essence the effect of increasing the annealing temperature on melting point and crystallinity is similar to, but less dramatic than that of

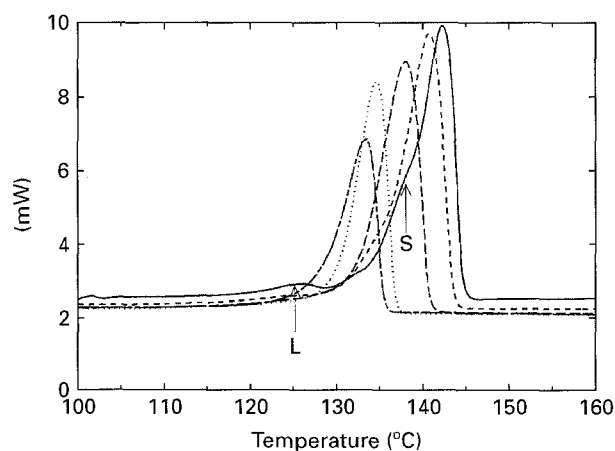


Figure 3 DSC melting endotherms of anabarcally annealed polyethylene. All samples annealed at 234°C and the stated pressure for 1 h. (—) 450 MPa, (---) 480 MPa, (· · ·) 515 MPa, (- · -) 540 MPa, (- - -) 585 MPa. S, shoulder; L, low-temperature peak.

reducing pressure. This similarity in behaviour extends to the more subtle changes in the shape of the melting endotherm. At annealing temperatures above 234°C the melting point of the polymer remains relatively constant, but a small endotherm and a low-temperature shoulder begin to appear. The final processing parameter, time, considered in set 3, has little effect on both the melting point and the crystallinity for times in excess of 15 min, although the values in Table I suggest that changes are far from complete by 5 min.

Two samples, set 4, annealed at pressures below the triple point close to the melting point, were also prepared to assess the importance of involvement of the hexagonal phase. A time of 1 h and a temperature of 180°C were chosen for both samples. Only the annealing pressures, 180 and 200 MPa, were different.

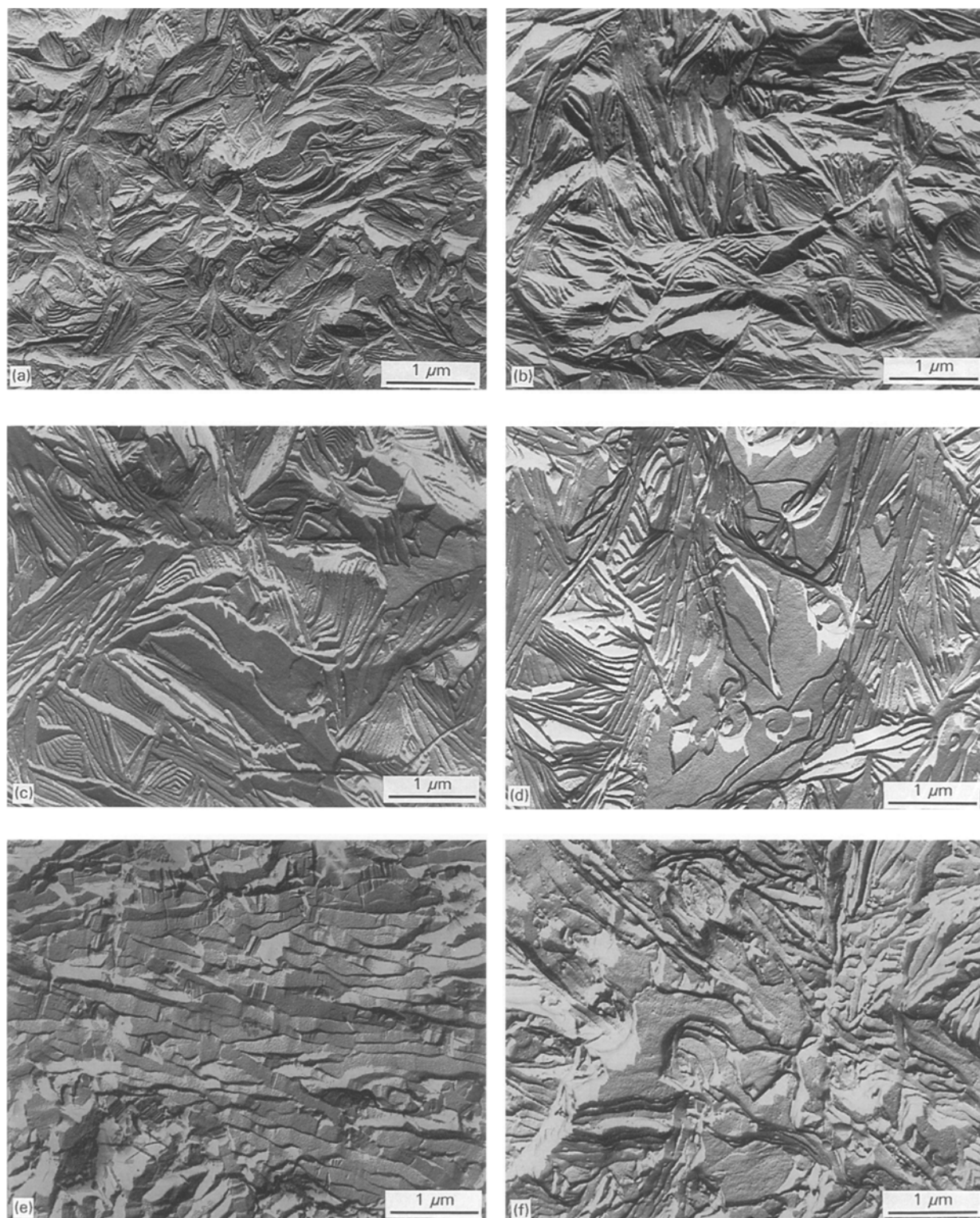


Figure 4 Transmission electron micrographs of anabarically annealed polyethylene. All samples were annealed at 234 °C and the stated pressure for 1 h, except where stated. (a) Conventionally melt-processed material, (b) 585 MPa, (c) 540 MPa, (d) 500 MPa; (e) 450 MPa, and (f) 500 MPa, 15 min.

Table I shows the results of DSC measurements on these samples. Clearly, the increase in the melting point of these samples is much smaller than that observed when annealing was performed at pressures above the triple point, in the diffuse boundary region (broadened by variation in lamellar thickness) where the orthorhombic and hexagonal phases are in equilibrium. Note also that for these samples, the changes occur almost at constant crystallinity, in marked

contrast to the behaviour at the higher pressures of Table I.

3.2. Transmission electron microscopy

Micrographs of samples produced following the isothermal path into the hexagonal phase are shown in Fig. 4. Fig. 4a shows the typical lamellar morphology

of the starting material which has been conventionally melt processed at atmospheric pressure. This original morphology is already transformed in material taken to the reference point (position J in Fig. 1) as in Fig. 4b, and the increased dimensions of the lamellae observed edge-on shows directly that lamellar thickening has occurred. The progressive change in morphology and lamellar thickness from this chain-folded plate-like structure to the stacked sausage appearance, familiar from earlier studies of high-pressure annealing (produced by recrystallization within the hexagonal phase [17]), is clearly apparent in Fig. 4b–e. Fig. 4d and f show micrographs of specimens annealed at 500 MPa, close to the orthorhombic/hexagonal phase boundary, for 60 and 15 min. The morphology is more obviously chain-extended in Fig. 4f, probably because of underlying variability in the annealing conditions. Generally, the morphology obtained in the region between 500 and 520 MPa is very sensitive to slight changes in the operating conditions and can show either or both types of structure. For this reason the morphology of these samples is referred to as transitional.

Table I indicates general classifications for the morphology obtained from TEM. Also included are values of the mean lamellar size obtained from measurements on lamellae presenting a suitable disposition to the direction of viewing in TEM. These data confirm the pronounced lamellar thickening and again indicate that changes are occurring over a range of pressures.

3.3. Nitric acid etching and GPC

An alternative means of determining lamellar thickness, used substantially in earlier work on polyethylene [14], is to use gel permeation chromatography to determine the length of the molecular stems left after nitric acid etching; this method is applied to the bulk of a sample rather than a surface. The peak, number, A_n , and weight, A_w , average molecular lengths obtained by this method are shown in Table I; to obtain lamellar thickness values, these have to be corrected for chain inclination, with multiplication by $\cos(34.5^\circ)$. Several observations noted from TEM measurements are also apparent here. First, the move to lower annealing pressures results in an increase in the lamellar size, although again the changes occur over a range of pressures. Secondly, the material annealed at the reference point J (585 MPa) has considerably thicker lamellae than the conventionally melt-processed starting material (sample R).

Set 3 in Table I lists results for stem-size measurements in samples subjected to different annealing times. The value for 15 min appears to be anomalously high, but this is most likely to be an indication of slight variations in experimental conditions (irregularities in the thermal history or pressure drop) having a very large effect in this transitional region close to the orthorhombic/hexagonal boundary.

3.4. Modulus

For comparative purposes, the 10 s isochronal creep bending modulus has been measured on samples ex-

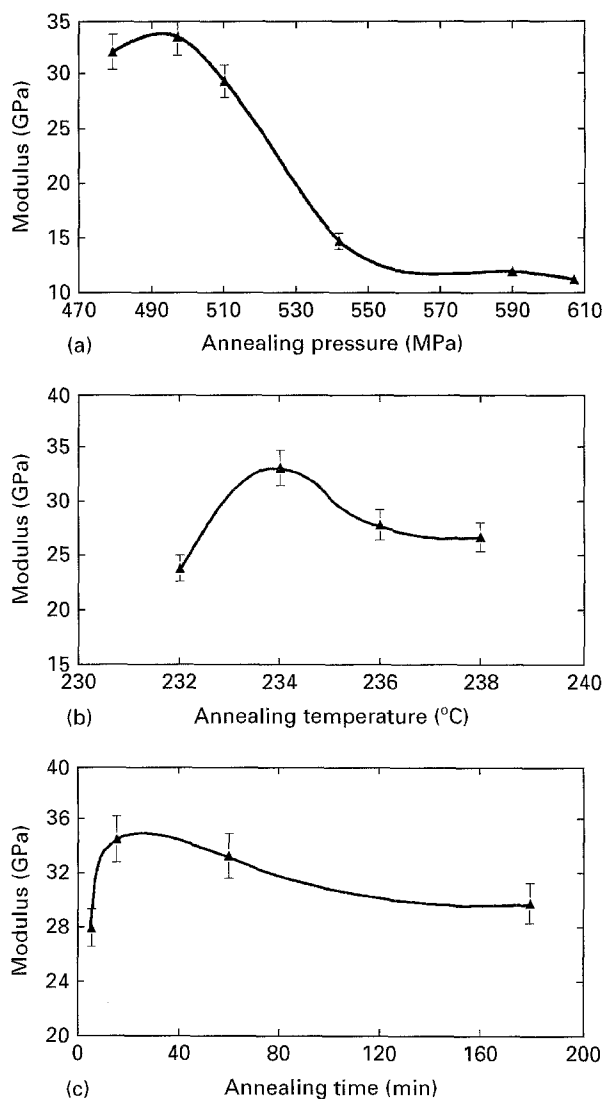


Figure 5 Variation of bending modulus of polyethylene extrudates as a function of anabarc annealing conditions. All samples were annealed using two of the standard annealing conditions, 500 MPa, 234 °C and 1 h, and the dependent variable, before being extruded to a fixed deformation ratio of 7. (a) Pressure, (b) temperature, (c) time.

truded to a standard extension ratio of 7. The different values for the several specimens therefore reflect the suitability of the various starting morphologies for obtaining improved modulus. The effects of varying the annealing parameters in turn are displayed in Fig. 5. As the annealing pressure is reduced at 234 °C, taking the polymer closer to the hexagonal phase, Fig. 5a, there is an increase in the modulus. The maximum value, 33 GPa, is achieved at annealing pressures between 500 and 480 MPa, and below this the modulus appears to fall. Values for the modulus of samples annealed at pressures below 480 MPa are not given, as these samples are incoherent and therefore difficult to characterize.

Fig. 5b shows the effect of changing the annealing temperature on the final properties. There is clearly a sharp increase in modulus as the annealing temperature is increased from 232 °C to 234 °C, but at higher annealing temperatures the modulus falls. It is difficult, however, to determine accurate values for the bending modulus of samples annealed at temperatures

above 234 °C, as these samples are partly incoherent. Increasing the annealing temperature has a very similar effect on the mechanical properties to that produced by reducing the annealing pressure. This is not unexpected, because both of these processes take the polymer towards and into the hexagonal phase.

The influence of the annealing time on the mechanical properties of the extrudate is shown in Fig. 5c. The increase in modulus with annealing times up to 15 min, and the slight fall at higher times, may reflect the anomaly in experimental conditions inferred from the nitric acid etching/GPC results. It should be pointed out, however, that for annealing times longer than 5 min, the effect of the annealing time on the modulus is only of secondary importance compared with varying the annealing pressure.

4. Discussion

The present paper reports a means of achieving reasonably high modulus (> 30 GPa) in polyethylene at modest extensions ($\times 7$) by a novel route involving high-pressure annealing of the precursor then orienting at 100 °C at atmospheric pressure. The main issues to discuss concern firstly, the morphologies developed by this annealing route; secondly, the consistency of the techniques for determining the molecular and morphological features so developed; and thirdly how these factors contribute to the success of this route in contrast to the weaknesses encountered previously with polyethylenes annealed at high pressure.

4.1. Transformation of the morphology

The principal effect of high-pressure annealing on linear polyethylene is the generation of thicker lamellae. Early work has shown that, in both oriented [18] and unoriented [17] forms, there is a continuous increase in average lamellar thickness with temperature and, to a lesser extent, time [19]. In this work, the same effect was also produced by a reduction in the annealing pressure. This familiar phenomenon, occurring substantially via local melting and recrystallization, assisted by solid-state thickening, will operate in both orthorhombic and hexagonal phases. Any discontinuity in thickness will be masked partly because of the broadening of phase transitions by crystal thinness, in the way familiar from polymeric melting endotherms and partly because of the suppression of thickening at high pressure produced by a restrictive lamellar environment [20]. All these factors will act in combination within the observed continuous monotonic increase in average thickness. The values > 100 nm which are produced reflect both the low enthalpy of fusion and the enhanced chain translational mobility of the hexagonal phase.

The broadening of the phase transitions, for the reasons outlined above, and further complications such as molecular weight effects, are probably sufficient to account for the observed transitional morphology of samples annealed at about 500 MPa, including the large variations seen among the specimens for small changes in processing conditions. At pressures

above 500 MPa, the samples are still in a recognizably chain-folded state. However, they have attained a high degree of crystallinity (noticeably greater than the samples treated around 180 or 200 MPa) and on extrusion a high modulus is developed. Large variations are seen among the specimens annealed at 500 MPa; these are likely to be due, not to the different annealing times, but to the aforesaid uncertainties in the position of the phase boundary.

As the annealing pressure is reduced from 500 MPa to 450 MPa, evidence of molecular weight effects is seen in the DSC traces where both the small low-temperature endotherm and shoulder on the side of the main melting peak (Fig. 3) become more prominent. The small peak at about 125 °C, has been identified with the formation of segregated regions of low molecular weight chains within the sample [18]. These low molecular weight chains, originally contained within the orthorhombic lamellae, are unable to be accommodated within a hexagonal crystal and are therefore rejected from the transforming lamellae. Rejected from the crystal, they segregate to positions between the chain-extended lamellae and on cooling they recrystallize directly into the orthorhombic phase as thin chain-folded lamellae, giving rise to the low-temperature endotherm upon re-melting. Previous experiments have shown that any chains with a molecular weight of less than 4000 will be rejected from the hexagonal crystal [17]. A similar explanation accounts for the development of the shoulder, but here involves molecules between 4000 and 10 000, which can enter thinner crystals of the hexagonal phase [17] during the increase in pressure as the specimen is returned to the reference position.

4.2. Measurement of lamellar thickness

Measurements of the extent of lamellar thickening have been made using both TEM measurements and the combination of nitric acid etching and GPC. These two techniques give somewhat similar values of the same quantity; the major reason for the small discrepancies is the inclusion of chain ends in the hexagonal crystals [21]. In addition, the Gibbs–Thomson equation, written as

$$\frac{1}{l} = \frac{\Delta h}{2\sigma_e} \left(1 - \frac{T}{T_m^0} \right) \quad (1)$$

where σ_e is the surface free energy of a chain-folded surface, Δh the enthalpy of fusion per unit volume, and T_m^0 the melting temperature of an infinite crystal, predicts a linear relation between the inverse of the lamellar size, l , and the melting point, and can be used to derive the lamellar thicknesses corresponding to the increase in melting point after annealing [18]. Such a relation is obtained when either the number or the weight average molecular stem lengths are plotted against melting point, as shown in Fig. 6. Extrapolation of these plots to infinite crystal size yields a value for T_m^0 of about 142.2 °C (weight average) or 142.4 °C (number average). Taking a value of 290 J g⁻¹ for Δh , the slope of the plot gives values for surface free energy

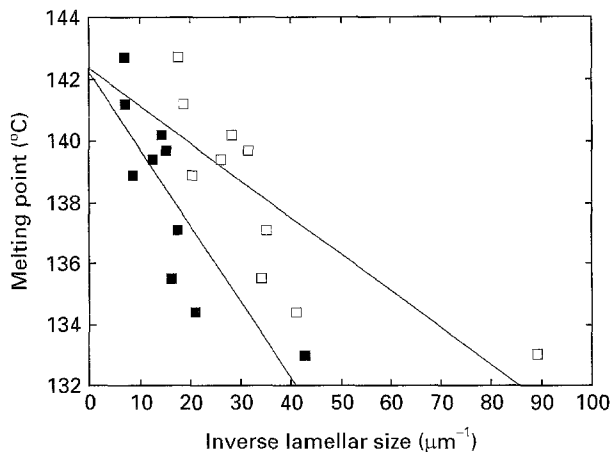


Figure 6 Inverse lamellar size from etching as a function of melting point. Lamellar size obtained from (□) number, and (■) weight averages.

of 86.8 mJ m^{-2} (weight average) or 42.2 mJ m^{-2} (number average). The weight average values are preferable a priori for at least three reasons. Firstly, they represent a sampling of the specimen partitioning according to the mass of the component parts. Secondly, the nature of the nitration/GPC method means that the chain extension will be systematically reduced whenever chain ends are included in crystals [21]. The weight average figure will suffer less from this effect than the number average. Thirdly, because melting point varies as the inverse of lamellar thickness, Equation 1, the maximum of the DSC peak will occur for the higher values of the length population for which the weight average is the more appropriate measure. The values given by the weight average are typical of a high-density polyethylene similar to HD6007EA. If superheating occurs, it is very limited in extent, and it is more to be expected with high molecular weights or very thick crystals [22,23]. Indeed, more detailed measurements on sample B revealed that a superheating correction of about 3 K needs to be applied to the chain-extended B, whereas none needs to be applied to the chain-folded E.

A more complete comparison of the different measures of lamellar thickness using results from DSC, TEM and etching experiments, is given in Fig. 7. Generally, there is a relatively good correlation between the different measurements of lamellar thickness, except that at low annealing pressures, the peak melting points obtained using DSC are excessively high, to the extent that for sample A, the peak is above the chosen T_m^0 . It should be remembered, however, that these are not equilibrium melting points, and are subject to superheating of a few degrees, especially at higher lamellar thickness. Caution must therefore be exercised in converting melting points to thicknesses, particularly for higher values where there is great sensitivity to the parameters applied to the Gibbs-Thomson equation. The real strength of the DSC is its ability to reveal the lower melting segregated populations.

The three different techniques clearly confirm that, at annealing pressures about 500 MPa and a temper-

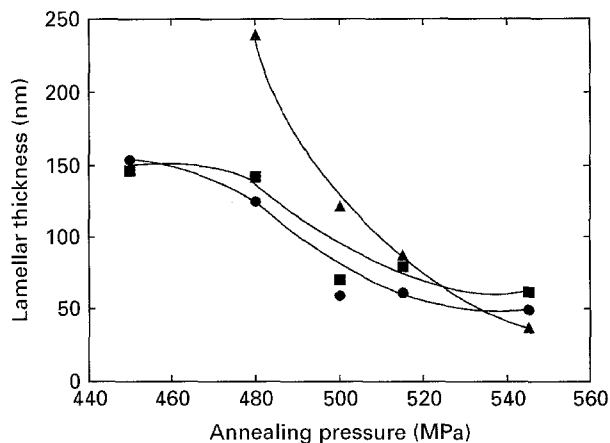


Figure 7 Comparison of lamellar thickness measured by: (▲) DSC, (●) TEM, and (■) GPC.

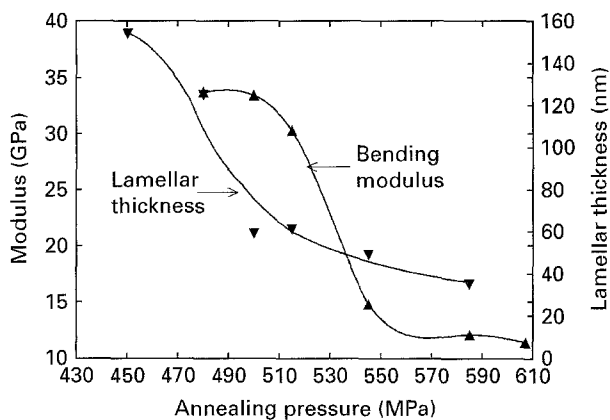


Figure 8 Comparison of changes in lamellar size, obtained from TEM, and extrudate modulus as a function of annealing pressure. All samples were annealed at 234°C and the stated pressure for 1 h. Extrudates deformed to an extrusion ratio of 7.

ature of 234°C , pronounced lamellar thickening can be achieved by small reductions in the annealing pressure (and small increases in temperature). Results for set 4 in Table I show that no significant changes are observed in either the crystallinity or the melting point of these samples, which have been annealed at a pressure below the triple point. The significant improvement in lamellar size is only produced when annealing is performed above the triple point, in the vicinity of the hexagonal phase.

4.3. Mechanical behaviour

The above sections have been concerned with the effect of annealing on the morphology of the isotropic material. Fig. 8 shows how the mechanical measurements on extruded material show a pronounced sensitivity to the annealing process, and consequently the pre-extrusion morphology. With this grade of polyethylene the modulus reaches a peak well before the lamellar size has reached the values of 100 nm or more, traditionally associated with annealing within the hexagonal phase; instead there is a clear maximum in the bending modulus for samples annealed at about 500 MPa and 234°C , i.e. where chain-folded morphology starts to give way to chain-extended morphology.

Samples which have been annealed at lower pressures and show chain-extended morphology, are totally incoherent and break up on attempts to extrude them. Furthermore, sample C, which shows the second highest modulus, has a pre-extrusion morphology with a lamellar thickness which could have been achieved by slow crystallization from the melt at atmospheric pressure, directly into the orthorhombic phase [24].

The fundamental issues involved in the pursuit of high modulus in crystalline polymers were highlighted by Frank [25]. High chain orientation is imperative; in addition there must be a compromise between high chain extension and toughness. The molecular chain-folding typical of crystalline polymers interrupts the covalent bond sequences, giving lower stiffness but especially when associated with a disordered region will also promote toughness by blunting any incipient cracks. Increasing chain extension will tend to increase both transverse and longitudinal weakness because of declining covalent connectivity. This will be lost, transversely, with chain-folding but the longitudinal behaviour depends upon the location of chain ends and whether these form lamellar surfaces. If they do, the bond sequence will be interrupted and the sample prone to failure. In this regard it is well known that crystallization at high pressure, commonly 500 MPa, substantially increases lamellar thickness but at the expense of toughness, usually giving a very friable product.

An early attempt to optimize mechanical properties sought to increase lamellar thickness progressively within oriented fibres by annealing at successively higher temperatures and constant length at 500 MPa [26]. In the event, toughness was not long retained and brittleness set in just above the orthorhombic/hexagonal transition because of the segregation of short molecules ($\geq 10^4$ daltons) into geometrically ordered arrays of flaws [27]. The prior extraction of this low molecular population restored ductility but, for typical polymer of $\sim 10^5$ daltons, only for tension along the fibre axis [28]. Specimens cut at 15° or more to this axis still failed, by shear in $\{hk0\}$ planes. Samples of the same material also tended to fail in compression down the orientation axis, either cleaving in $\{hk0\}$ planes and/or forming kink bands. Prone-ness to failure was, however, absent from Hifax 1900 with a higher molecular weight ($> 2 \times 10^6$ daltons) from which it was concluded that sufficient molecular continuity to maintain ductility required a ratio of molecular length, L , to crystal thickness, l , greater than 10, the value for typical polyethylenes ($\sim 10^5$ daltons) with lamellae 100 nm thick.

It is interesting that the processing employed in the present work is markedly more successful in terms of mechanical properties of the product than were the earlier studies, even though the molecular weight and crystal thicknesses employed are similar. This points firmly to the influence of solid-state extrusion on the underlying molecular network in restoring toughness to what would, on the basis of its molecular length and crystal thickness alone, have been expected to be a brittle product.

For the purposes of these experiments it is possible, therefore, to increase overall crystal thickness continuously at constant molecular length with corresponding effects for the underlying molecular network. The increasing thickness implies a contraction in the lateral range of a molecule with a corresponding tendency to reduce lateral strength. The thicker the lamellae and the more organized the fold surfaces, the greater is the tendency to failure. However, the condition of the fold surface regions is a major factor in producing toughness because chain-extended lamellae have been observed to undergo c shear by the whole stem length, principally in $\{200\}$ planes, with additional deformation limited by the molecular continuity in the fold surfaces [29]. This obviously raises questions on the importance of the hexagonal phase for producing high-modulus samples. Results from this and other grades of polyethylene make it appear more likely that the achievement of an optimum lamellar size for a particular grade is mainly responsible [30], and that the detrimental effect on the network of enhancing the crystal size beyond a certain level limits the benefits of annealing within the hexagonal phase [12].

The nature of the best compromise obtained in practice, therefore, provides novel insight into the morphological and network conditions which give optimum fibre properties. The molecular weight of the polymer will clearly be an important factor; this is explored further in the following paper.

5. Conclusion

The morphology of anabarically annealed polyethylene samples has been shown to be highly sensitive to the annealing conditions, especially in the vicinity of the orthorhombic/hexagonal boundary. The modulus of these samples, when extruded to a standard deformation ratio, reflects differences in the morphology of the starting material. For this medium molecular weight material, the highest modulus is not obtained by annealing within the hexagonal phase but rather on the border between it and the orthorhombic phase. Although the lamellar size is dramatically increased by annealing within the hexagonal phase this development tends to occur at the expense of the integrity of the molecular network. Beyond a certain value, samples become increasingly incoherent and the modulus of the extrudates falls.

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