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The effect of molecular weight on the deformation behaviour of pressure annealed polyethylene

A. S. MAXWELL, A. P. UNWIN, I. M. WARD
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK
M. I. ABO EL MAATY*, M. M. SHAHIN†, R. H. OLLEY, D. C. BASSETT
J. J. Thomson Physical Laboratory, Whiteknights, University of Reading, Reading RG6 6AF, UK

The deformation behaviour of four different grades of polyethylene has been examined as a function of the morphology produced by pressure annealing in the vicinity of the orthorhombic–hexagonal phase boundary. It is concluded that annealing within the hexagonal phase, to produce a "chain-extended" morphology, is appropriate for high molecular weight material as a precursor step in the production of high modulus by solid phase deformation. In low molecular weight material of the same morphology solid phase deformation does not produce improvements in mechanical behaviour. These results are interpreted in terms of the competition between increasing crystal size and the decrease in the coherence of the molecular network brought about by the pressure annealing. The critical parameter is the ratio of lamellar size to number average molecular chain length, rather than lamellar morphology. When this parameter is greater than 0.5 the molecules are incapable of completing two crystalline traverses and the network is affected detrimentally to the extent that it no longer holds the material together.

1. Introduction

Early work by Capaccio *et al.* [1] emphasised two factors which determine the solid phase deformation behaviour of crystalline polymers; namely the extension of a molecular network, which is common to both amorphous and crystalline polymers and the morphology of the sample, which is critically related to the rate of initial cooling from the melt, i.e., the crystallization conditions. In the present paper these ideas are developed and extended for pressure annealed polyethylene.

The lamellar morphology produced by the high pressure annealing of polyethylene depends critically on the proximity of the annealing conditions to the orthorhombic–hexagonal phase boundary. Two extreme morphologies are well known and commonly termed chain-folded and chain-extended. They have been shown [2] to result from crystallization into the orthorhombic and hexagonal phases respectively. The chain-extended morphology is also realized by annealing within the hexagonal phase when there is substantial, not merely local, melting and recrystallization. Between these two extremes the lamellar thickness and lamellar morphology change continuously [3] and for convenience, the morphology may be termed transitional.

This visual characterization, although historically very important, is only one aspect of the morphology, and to some extent masks other more subtle changes in the makeup of the material. The phase structure of different polyethylene specimens when probed by ^{13}C NMR (nuclear magnetic resonance) techniques has revealed three components, namely a crystalline phase, an "interphase" at the surface of the crystals, and a proportion of rubbery-amorphous phase which increases as a function of molecular weight [4]. Crystallization from the melt into the hexagonal phase reduces the proportion of the rubbery-amorphous phase; furthermore, the molecular weight above which this phase starts to appear is higher. During high pressure treatment crystallinity and lamellar size increase at the expense of the rubbery-amorphous phase. This change to thicker crystals must increase the separation of nodes of the network and is thereby potentially significant as a means of reducing the restrictiveness of the molecular network to a point where it does not impede the development of orientation during subsequent deformation. However, excessive crystal thickening may go so far as to affect the network (and sample) integrity detrimentally, so some optimum balance is required.

Evidence of the potentially critical nature of the competition between increasing crystal size and the decrease in the coherence of the molecular network comes from previous work. Mead and Porter [5] and Chuah and Porter [6] observed that, when annealed

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On leave from Faculty of * Engineering and † Department of Physics, Al-Mansoura University, Al-Mansoura, Egypt.

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TABLE I Polyethylene grades subjected to pressure annealing

Grade	Polymer	Source	Process	$\bar{M}_w$	$\bar{M}_n$
A	HD6007EA	BP chemicals	Moulded	135 000	25 500
B	H020 54P	BP chemicals	Compacted	312 000	33 000
C	R516	BP chemicals	Compacted	742 000	13 600
D	GUR412	Auhrchessie	Compacted	4500 000	–

within the hexagonal phase, low molecular weight material could not be oriented to give satisfactory improvements in mechanical behaviour. Using a slightly higher molecular weight material, Powell *et al.* [7] concluded that annealing within the hexagonal phase generated a material which was suitable for extruding to high modulus. A more detailed examination of the same grade of material [8] showed that the ideal morphology was of the intermediate type, produced by annealing on or about the phase boundary. Annealing well within the stable region of the hexagonal phase was detrimental to mechanical improvement. In this paper the factors which determine the optimum morphology are investigated by examining several different molecular weight grades of polyethylene. The morphology produced by pressure annealing is examined in detail and its suitability for mechanical enhancement monitored by measuring the modulus of extrudates subjected to identical deformations.

2. Experimental procedure

Four different grades of high density polyethylene homopolymer, whose molecular weight characteristics are outlined in Table I, have been examined. For each of these grades, samples displaying a range of morphologies have been prepared by annealing at successively higher pressures, above 315 MPa where the hexagonal phase intervenes between the normal orthorhombic phase and the melt [9]. For all but grade A this involved the preliminary step of powder compaction in a hydrostatic pressure vessel at a temperature of about 160 °C and a pressure of 200 MPa. This pressure was then reduced to about 40 MPa to permit some melting of the material, and maintained there for about 15 min. The precise conditions in this sintering step were chosen to ensure that the final compact possessed adequate mechanical integrity to withstand subsequent machining.

The compacts were machined into small rods and then pressure annealed in a special pressure vessel. Details of both apparatus and procedure are as outlined for the annealing of the melt extruded rods of grade A, described elsewhere [8]. This earlier paper explored in detail the effects of varying pressure, temperature and time in the annealing stage. The annealing pressure and temperature were shown to have a more dominant influence than the time, and of these the pressure afforded easier and more reliable control. Consequently, only morphologies obtained by varying this parameter are considered here. In all cases the annealing temperature and time are fixed at 234 °C and 1 h respectively. These conditions, together with a pressure of 500 MPa, correspond to these required to produce the optimum morphology in grade A, which for this material was intermediate between the "*chain-folded*" and "*chain-extended*" types.

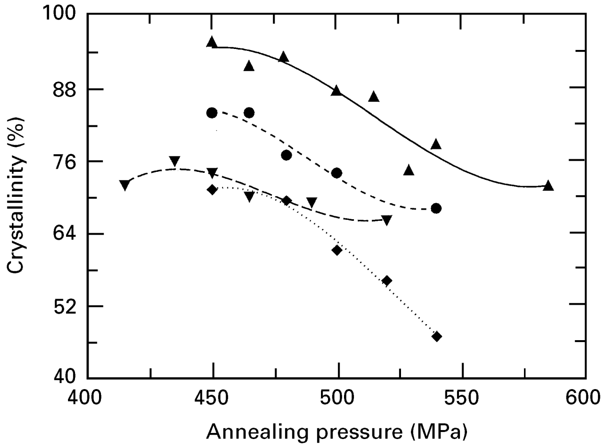

Figure 1 Variation in crystallinity as a function of annealing pressure for four grades of polyethylene. (▲) A; (●) B; (▼) C; and (◆) D. All samples annealed at 234 °C and stated pressure for 1 h.

The morphology of those isotropic samples after pressure annealing was characterized using differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Most DSC traces of the melting behaviour were obtained at a heating rate of 10 K min^{-1} using a Perkin Elmer DSC7, although slower heating rates were also used to investigate superheating. TEM micrographs, yielding lamellar thicknesses and morphological characterization, were obtained from surfaces etched with a permanganic reagent [10] and replicated. The rod shaped samples were also hydrostatically extruded at 100 °C to a standard nominal draw ratio of 7 (final diameter of 1.8 mm). The ten second isochronal modulus at 20 ± 3 °C, measured in three point bend on samples of aspect ratio greater than 40, was used to assess the suitability of the morphology for producing large improvements in modulus.

3. Results

Fig. 1 shows the variation in crystallinity as a function of annealing pressure in each of the four grades. As the annealing pressure is reduced all grades show an increase in the crystallinity. The behaviour is similar to that already reported [8] for grade A, with the major increases occurring over a relatively narrow range of pressures. The annealing pressures at which these

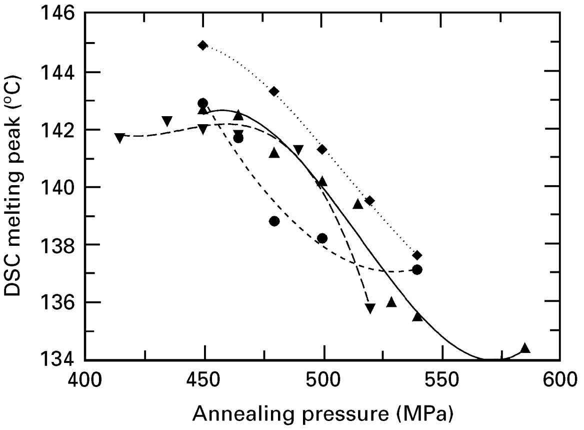

Figure 2 Variation in peak melting point as a function of annealing pressure for four grades of polyethylene. (▲) A; (●) B; (▼) C; and (◆) D. All samples annealed at 234 °C and stated pressure for 1 h.

pronounced changes occur are similar for each grade, with a slight shift to lower pressures as the molecular weight is increased. The maximum crystallinity developed during annealing is also lower in the higher molecular weight materials.

The corresponding variations in melting point, shown in Fig. 2, are very similar to those for the crystallinity. These results have been obtained at a heating rate of 10 K min^{-1}, and include a superheating effect which increases with lamellar size and molecular weight. The highest molecular weight, grade D, shows the greatest superheating leading to its very high observed melting point. Crystallinity values are insensitive to heating rate.

Several other differences between grades are manifested in the melting curves. When the lowest molecular weight, grade A, is annealed at pressures below 500 MPa a second smaller endotherm appears at temperatures of around 125 °C and a large shoulder develops on the low temperature side of the main melting peak. These developments become more pronounced as the annealing pressure is reduced. A typical melting trace is shown in Fig. 3(a–d) which also shows traces obtained from each of the other grades annealed under identical conditions. Clearly, as the molecular weight increases the tendency for the small low temperature endotherm and the shoulder to form at these annealing conditions is reduced. Indeed the small low temperature endotherm only forms at the lowest annealing pressure; in the highest molecular weight, grade D, it did not appear in any of the annealed samples.

This low melting peak is attributed [11] to the formation of a "segregated phase" of low molecular weight chains, and it has been shown that removal of short chain material from the polymer also removes the low temperature melting peaks [12]. It is probable that these short chains, originally contained within the orthorhombic lamellae, cannot be accommodated within the large hexagonal crystals and are therefore rejected from the lamellae as they convert into the hexagonal phase. Upon rejection they enter the molten state and segregate to positions between the hexagonal lamellae [13] recrystallizing there upon cooling in the form of thin chain-folded lamellae with a lower melting point. The decline of these low molecular weight fractions as the molecular weight is increased is no doubt responsible for the fall in intensity of the low temperature endotherm.

The tendency for the shoulder to decrease in higher molecular weight material also arises because of the removal of low molecular weight components. Its development has been attributed [3] to the fraction of

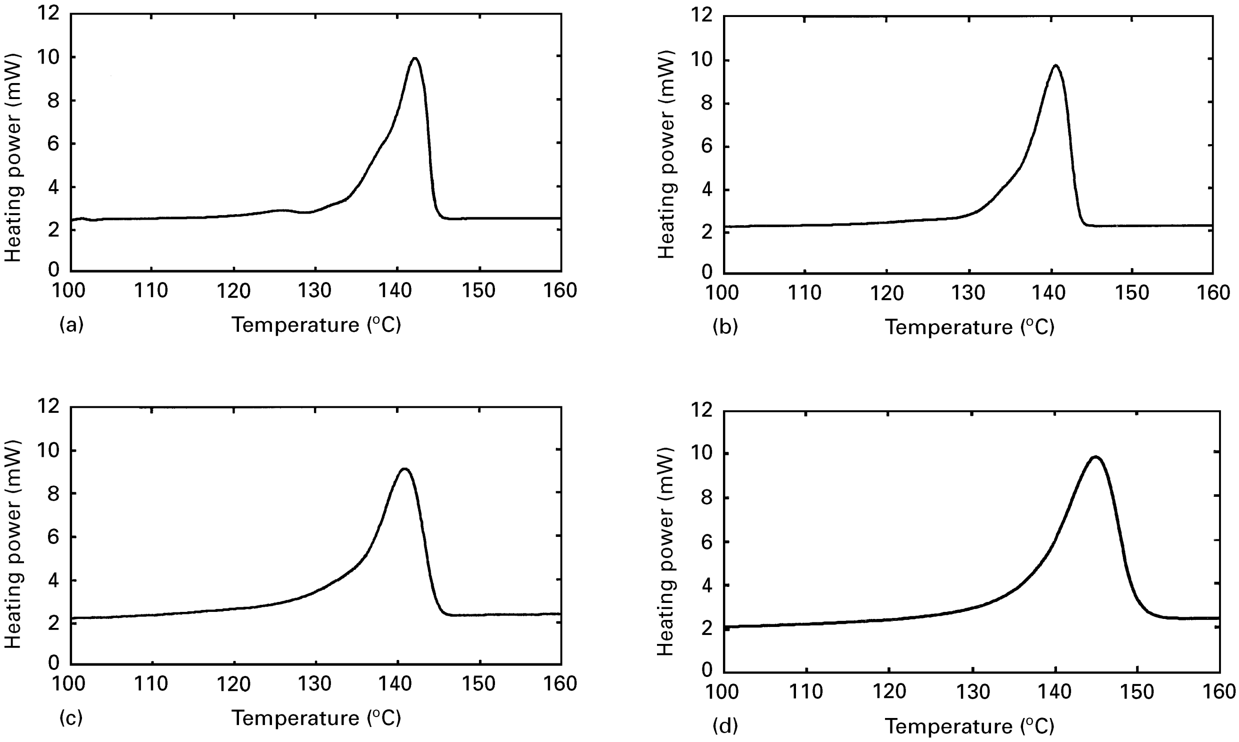

Figure 3 DSC melting endotherms of (a) A, (b) B, (c) C and (d) D grades of polyethylene. All samples annealed at 234 °C and 450 MPa for 1 h.

TABLE II The effect of varying the annealing pressure (at 234 °C for 1 h) on the morphology

Grade	Pressure (MPa)	DSC peak temperature (°C)	Crystallinity (%)	TEM morphology	Lamellar thickness (nm)
A	450	142.7	95.8	Chain extended	154
	480	141.2	93.3	Chain extended	125
	500	140.2	87.7	Transitional	59
	515	139.4	86.7	Transitional	61
	540	135.5	78.8	Chain folded	49
	585	134.4	71.8	Chain folded	20
B	450	142.9	84.0	Chain extended	70–120
	465	141.7	84.0	Chain extended	80–100
	480	138.8	77.0	Chain folded	40[b]
	500	138.2	74.0	–	–
	540	137.1	68.0	Chain folded	20
C	415	141.7	72.0	Chain extended	100–200[a]
	435	142.3	76.0	Chain extended	70–100
	450	142.0	74.0	Chain extended	60–80
	465	141.8	70.0	Chain extended	50–70
	490	141.2	69.0	Transitional	40–50
	520	135.7	66.0	Chain folded	20
D	450	144.9	71.3	Chain extended	70–100
	480	143.3	69.4	Chain folded	25–35
	500	141.3	61.1	Chain folded	25[b]
	520	139.5	56.0	–	–
	540	137.6	46.8	Chain folded	15

[a] See discussion relating to Fig. 7a for explanation of these results.

[b] See discussion relating to Fig. 7b for precautions needed in obtaining these results.

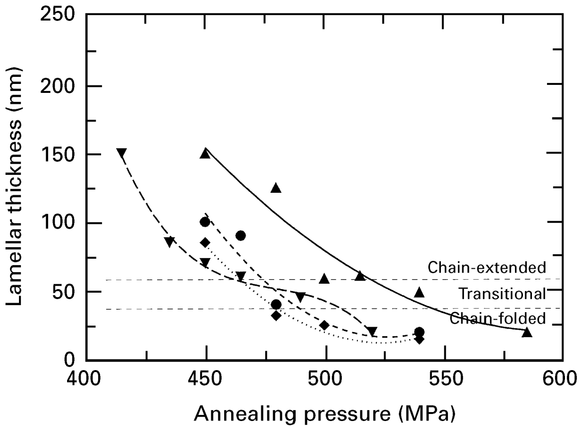

Figure 4 Variation in lamellar thickness, obtained from TEM, as a function of annealing pressure for four grades of polyethylene. (▲) A; (●) B; (▼) C; and (◆) D. All samples annealed at 234 °C and stated pressure for 1 h.

the material between 4000 and 10 000 Da which, having entered the melt during annealing, recrystallises rapidly during cooling into the hexagonal phase, but as thinner crystals with a slightly lower melting point.

TEM micrographs were obtained for the different polyethylene grades which had been subjected to a range of annealing pressures. Values for the average lamellar thickness together with a simple morphological classification are given in Table II while Fig. 4 compares the development of lamellar size, obtained from TEM, with annealing pressure in all four grades. This graph clearly shows an increase in the lamellar thickness in all of the grades as the annealing pressure is reduced. However, the annealing pressure required to produce a given lamellar thickness decreases as the molecular weight increases, corresponding to a somewhat deeper incursion into the stability region of the hexagonal phase.

Fig. 5(a–d) shows TEM micrographs of all four grades annealed at 450 MPa. At this pressure all samples show a considerably thickened lamellar morphology. Clearly there is a monotonic decrease in lamellar thickness with increasing molecular weight.

Fig. 6(a–d) shows the effects of annealing at higher pressure on the two extreme molecular weight grades. Fig. 6 (a and b) show that thinner crystals have resulted after a limited drop of pressure, to 540 MPa. A dramatic difference between the two extreme molecular weights is seen at 500 MPa where grade A (Fig. 6c) is thickened considerably while grade D (Fig. 6d) is still comparatively thin. This is presumably a consequence of the sensitivity of the orthorhombic–hexagonal phase boundary to molecular weight [14, 15].

Fig. 7 (a and b) shows two effects due to the width of molecular weight distributions. In Fig. 7a, grade C has been taken to the very low annealing pressure of 415 MPa. Here, because of the very great breadth of the molecular distribution of this material, some segregation has occurred with thin lamellae, containing low molecular weight material, evident between the main lamellae. However, such segregation does not destroy the mechanical integrity of the sample as it does in grade A [8]. Presumably this is because the very long molecular end of the distribution is able to form a network which can encompass these segregated pockets.

Fig. 7b shows a very different kind of segregation in grade B. This did not occur during the high pressure treatment, but more probably during the pressing of the original billet. Most of the material is heavily

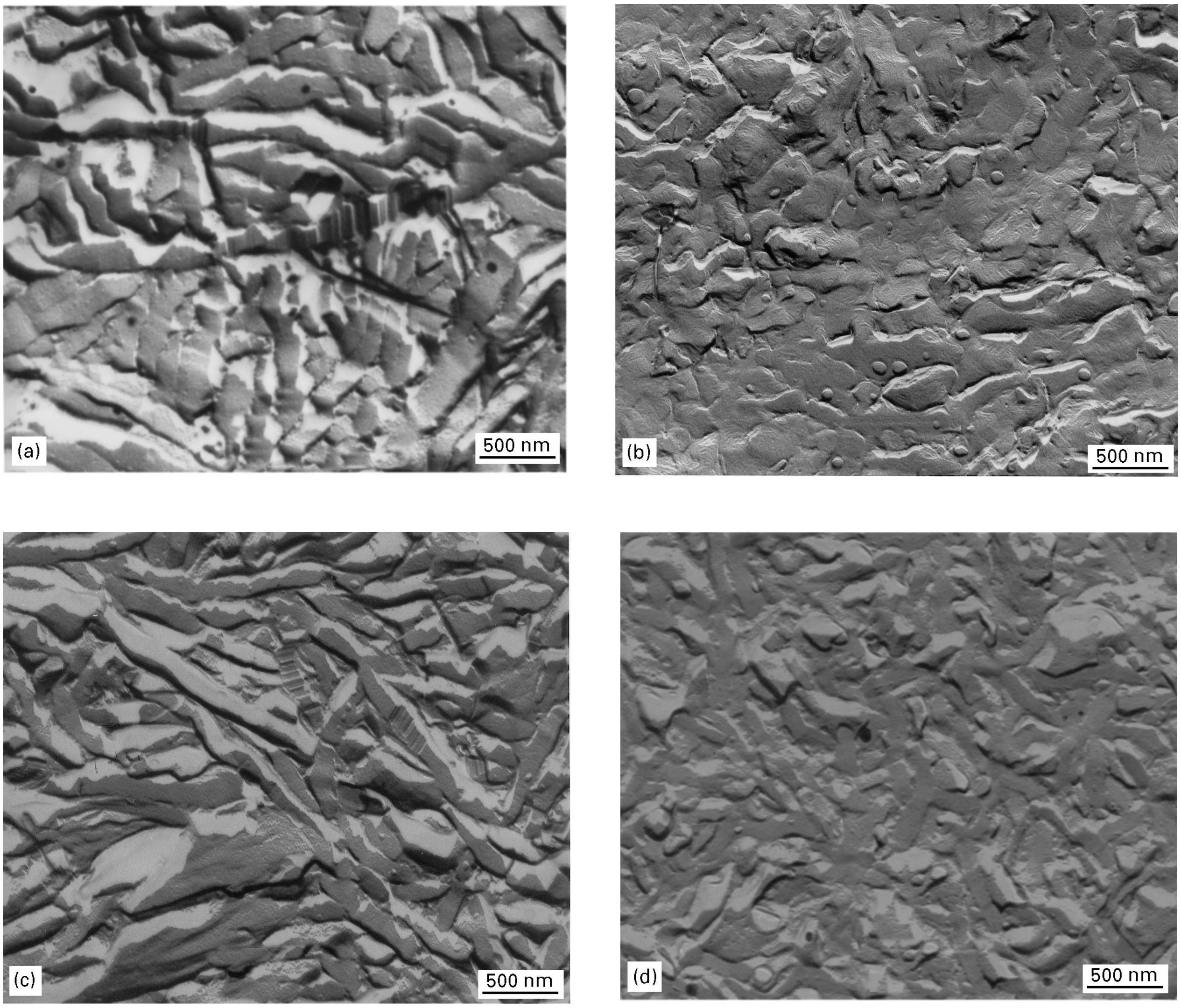

Figure 5 TEM micrographs of four grades of polyethylene (A to D as identified in Table I) after pressure annealing at 234 °C and 450 MPa for 1 h.

nucleated, but there are lightly nucleated pockets, several microns or more in size, where lower molecular weight has congregated during the compaction of the original powder. On subsequent high pressure annealing these develop a banded spherulitic texture (left of picture): higher magnification shows the lamellar thickness there to be slightly greater, in keeping with the idea that these pockets contain lower molecular weight material. These regions do not appear to destroy the mechanical integrity of the specimens, but nevertheless, procedures to avoid this behaviour should be developed if this material were to be used in any industrial processing.

Segregation effects are also found on a much smaller scale in material D. The original particles of such high molecular weight material have been shown to maintain their individuality even after high pressure treatment [4]. Material comprising the lower tail (less than 5%) of the molecular weight distribution migrates into the "tetrahedral" interstices where four of the quasi-spherical particles have been deformed together. Consequently, in a sample such as grade D annealed at 500 MPa, while the main body of the particles is composed of lamellae of thickness 25 nm, the interstices contain lamellae up to 40 nm thick. It is therefore important to avoid these untypical regions when estimating lamellar thickness by TEM.

Fig. 8 shows how the bending modulus of samples of identical deformation ratio depends on the annealing pressure. Initially, all four grades show an increase in modulus as the annealing pressure drops, but at lower pressures the modulus levels out or begins to fall. The existence of an optimum annealing pressure is implied, although its value varies from grade to grade.

4. Discussion

The results presented above illustrate a complex interrelation between the annealing conditions and the resultant morphology, on the one hand, and between morphology and its suitability for deformation, on the other. Thus the choice of a fixed set of annealing conditions can generate a range of crystallinities and lamellar size depending on the molecular weight of the material. In addition different degrees of segregation and morphological classification can also be produced. The suitability of these morphologies for solid phase deformation and the mechanical improvement thereby achieved are impossible to predict on a morphological basis alone, with low molecular weight

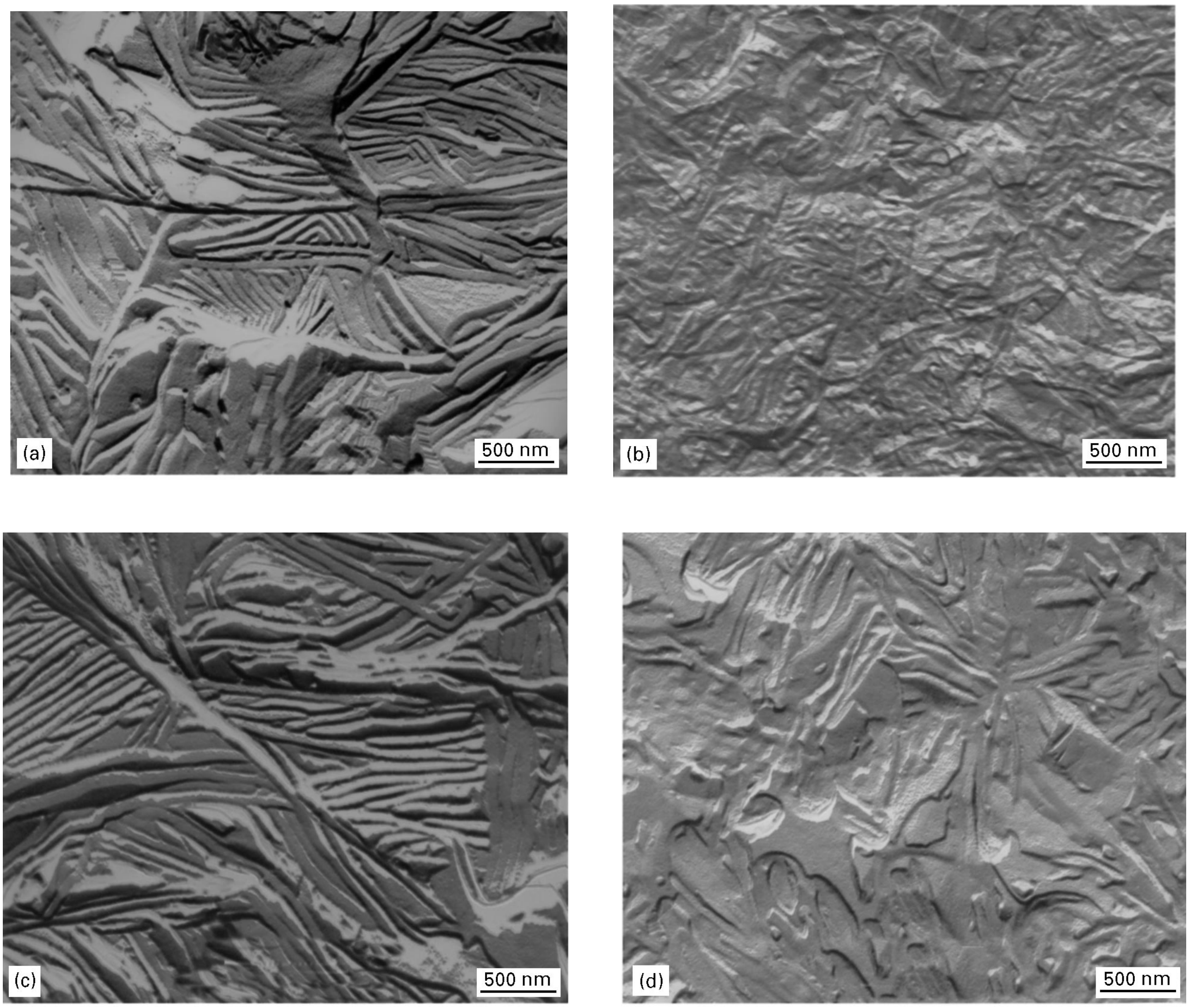

Figure 6 TEM micrographs of polyethylene annealed at the pressure stated and 234 °C for 1 hour; a) grade A, 540 MPa, b) grade D, 540 MPa, c) grade A, 500 MPa, and d) grade D, 500 MPa.

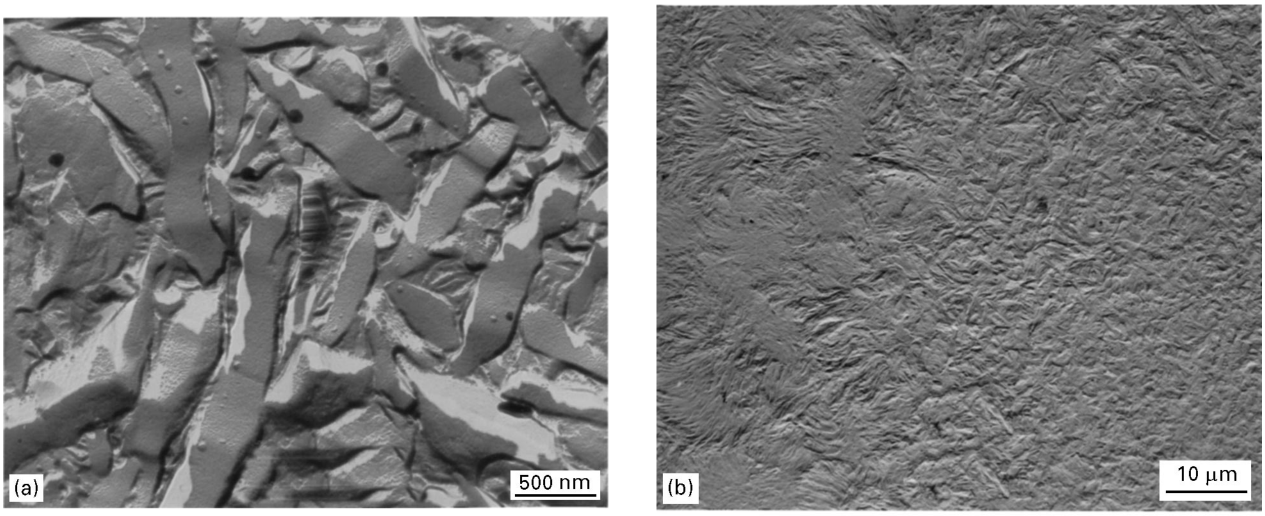

Figure 7 TEM micrographs showing evidence of segregation. a) Grade C after annealing at 234 °C and 415 MPa for 1 hour and b) Grade B after annealing at 234 °C and 480 MPa for 1 hour.

material in the chain-extended morphology being far inferior to high molecular weight in the same morphology.

As a starting point it is appropriate to consider the impact of annealing on the network. The increased levels of crystallinity and lamellar size that accompany the annealing [16] or crystallization [17] of polyethylene within the hexagonal phase necessitate a greater ordering of the molecules, presumably at the expense of molecular entanglements as molecules are withdrawn

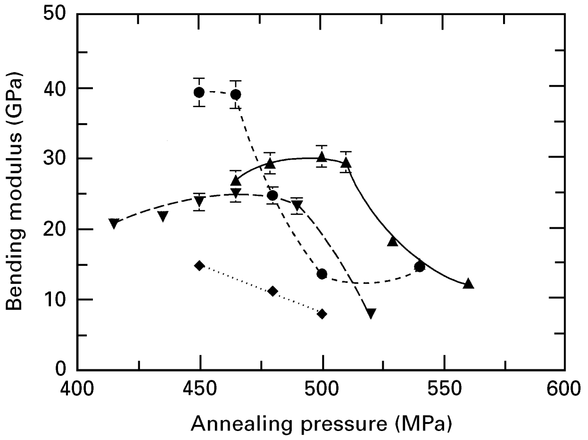

Figure 8 Variation in bending modulus of polyethylene extrudates as a function of annealing pressure. The four different grades correspond to (▲) A; (●) B; (▼) C; and (◆) D in Table 1. All samples annealed at 234 °C and stated pressure for 1 h before being extruded to a fixed deformation ratio of 7.

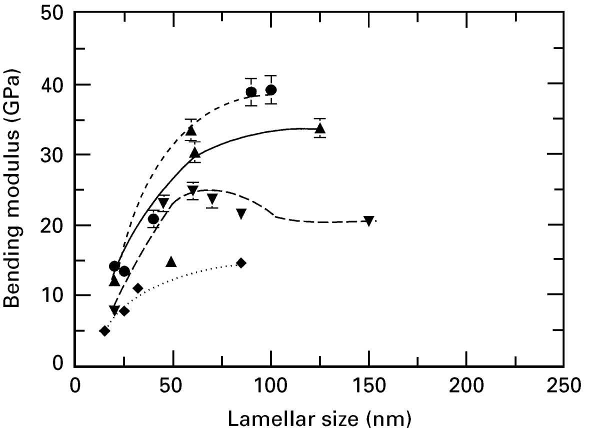

Figure 9 Variation in bending modulus of polyethylene extrudates as a function of lamellar size. The four different grades correspond to (▲) A; (●) B; (▼) C; and (◆) D in Table 1. All samples annealed at 234 °C for 1 h before being extruded to a fixed deformation ratio of 7.

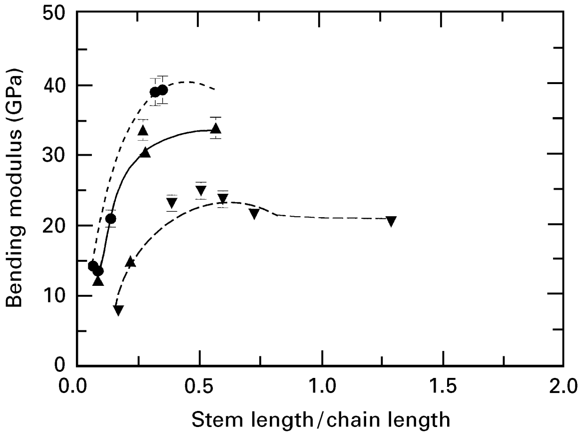

Figure 10 Variation in bending modulus of polyethylene extrudates as a function of the ratio $L/\bar{M}_n$. The four different grades correspond to (▲) A; (●) B; (▼) C; and (◆) D in Table 1. All samples annealed at 234 °C for 1 h before extruded to a fixed deformation ratio of 7.

from the network. The effectiveness of the network, examined in the oriented samples [18], decreases as the sample is annealed to progressively greater lamellar thicknesses. This is in agreement with work by Kitamaru *et al.* [4] on the pressure crystallization of different grades of polyethylene. They showed that the rubbery amorphous content, derived from NMR measurements of mobility, drops considerably when the material is pressure crystallized and that in medium molecular weight material ($\bar{M}_w \sim 10^5$) it is effectively absent.

Although pressure annealing does not develop crystal thicknesses quite as great as pressure crystallization and so is less effective than pressure crystallization in removing the rubbery amorphous component, the general conclusions reported by Kitamaru *et al.* are applicable here. The rubbery amorphous content of annealed samples will depend on factors including the annealing conditions, the molecular weight and probably also the initial entanglement density, itself dependent on the initial form, i.e., powder or pellet. A complete analysis may also reveal a sensitivity to the molecular weight distribution and in particular segregation arising from the different thermodynamic stabilities and kinetic characteristics of molecules of different length, but initially these potential complications will be ignored. The major restriction on the ability of a molecule to take part in the rubbery phase of a semicrystalline polymer is its finite length. Kitamaru *et al.* showed that the rubbery amorphous content effectively disappears when the ratio of the number average molecular length to the mean crystallite size is less than 2; that is when the crystal size is so large that a typical molecule cannot complete two crystalline traverses.

Fig. 9 shows how the modulus of all four grades, when extruded under identical conditions, varies with lamellar size. Generally the modulus increases with lamellar size although there is a particular value, dependent on the grade, above which there is a fall or no further improvement. It is also important to note that results from samples wih large lamellar size and which do not deform satisfactorily are not included in this figure because they cannot be measured owing to multiple crack like defects. If the lamellar size is considered in relation to the number average molecular length it is more appropriate to plot modulus against the ratio $L/\bar{M}_n$, where L is the lamellar thickness. This is done in Fig. 10. It is now noticeable that, irrespective of the grade, the modulus tends to peak at a value of $L/\bar{M}_n$ of about 0.5, which is the condition that Kitamaru *et al.* found to be coincident with the disappearance of the rubbery amorphous phase. If it is the number average which is important, this would imply that the chain ends are the effective agent in disrupting the network. But when considering mechanical integrity, it might also be considered that the rubbery amorphous phase is an effective agent, in blunting cracks and preventing their propagation. This relationship is not strictly comparable with the relationship $L/\bar{M}_w > 10$ required for avoiding fracture of oriented pressure annealed material [19]. Nevertheless this discrepancy does point to the conclusion that the method of pressure extrusion developed in this work is a significant improvement on previously studied orientation methods. Finally, the value of the maximum modulus does vary between grades and as is shown elsewhere [20] relates to crystallinity and orientation.

Clearly then, from the perspective of producing a morphology suitable for orienting to give high modulus, the rubbery amorphous phase must be retained and this is only achieved provided that the lamellar size is not allowed to exceed half the mean chain length. This critical dependence on the relative lamellar size and consequent network integrity indicates why annealing medium molecular weight material within the hexagonal phase has proved of little benefit when trying to achieve high modulus [5, 6]. The network integrity dominates over any morphological changes induced by annealing so that the latter cannot be used as a sole guide to the suitability of a sample for orienting. It is essential to use high molecular weight material if annealing is to be performed in the hexagonal phase. The additional entanglement density associated with such a move, however, restricts the development of crystallinity and crystallite size and consequently limits the overall benefit. This is seen more clearly by considering the effects of different annealing conditions on the four grades.

All grades show a change from conventional stacked chainfolded lamellar morphology to a so-called chain extended morphology as the annealing conditions are changed so as to move across the hexagonal–orthorhombic boundary. This is achieved by either reducing the pressure or increasing the temperature. Between these two distinct morphologies lies a transitional region associated with annealing on the phase boundary and probably arising because the position of the hexagonal phase depends on lamellar thickness [21] so that lamellae of different thicknesses enter the hexagonal phase at slightly different annealing conditions. The change is most abrupt in grade A. The relatively low polydispersity of this grade probably explains the narrow transitional band although good kinetics, favoured by a low entanglement density, may also play a part.

There is direct evidence of the orthorhombic–hexagonal transition temperature increasing with molecular weight [14, 15, 22]. Moreover, although their effect is not usually considered explicitly, it would be anticipated that higher entanglement densities would occur both for longer molecules and for melt-processing of initially powder compacted samples. The latter is consistent with observations of Yasuniwa *et al.* [15]. The former is a likely explanation of the data in Figs. 1, 5 and 6 showing that final lamellar thickness and crystallinity, achieved under constant annealing conditions, are lower for higher molecular weight polyethylene.

5. Conclusions

The implications of pressure annealing polyethylene in and around the hexagonal phase are clearly complex. Notwithstanding these complexities it can be inferred that:

(1) For successful extrusion it is essential that a rubbery amorphous phase is retained and this is only significant if the mean lamellar size does not exceed half the mean chain length.

(2) This implies that only high molecular weight material should be annealed within the hexagonal phase, otherwise the development of crystallite size occurs at the expense of the network integrity and samples become mechanically unsuitable.

(3) The move to higher molecular weights introduces a greater entanglement density which restricts the development of crystallinity. This in turn limits the values of modulus that can be achieved as these depend more critically on the morphology.

(4) The loss of network integrity can sometimes be identified by the appearance of segregation in the DSC melting endotherms. It has not been shown, however, that segregation always accompanies loss of network integrity.

References

1. G. CAPACCIO, A. G. GIBSON and I. M. WARD, in "Ultrahigh Modulus Polymers", edited by A. Ciferri and I. M. Ward (Applied Science, Barking 1979), Chapter 1.
2. D. C. BASSETT, S. BLOCK and G. J. PIERMARINI, *J. Appl. Phys.* **45** (1974) 4146.
3. D. C. BASSETT, B. A. KHALIFA and R. H. OLLEY, *Polymer* **17** (1976) 284.
4. R. KITAMARU, F. HORII, Q. ZHU, D. C. BASSETT and R. H. OLLEY, *ibid* **35** (1994) 1171.
5. W. T. MEAD and R. S. PORTER, *Int. J. Polym. Mat.* **7** (1979) 29.
6. H. H. CHUAH and R. S. PORTER, *J. Polym. Sci. Phys. Ed.* **22** (1984) 1353.
7. A. K. POWELL, G. CRAGGS and I. M. WARD, *J. Mater. Sci.* **25** (1990) 3990.
8. M. M. SHAHIN, R. H. OLLEY, D. C. BASSETT, A. S. MAXWELL, A. P. UNWIN and I. M. WARD, *ibid* (in press).
9. D. C. BASSETT and B. TURNER, *Phil. Mag.* **29** (1974) 925.
10. R. H. OLLEY, D. C. BASSETT, P. J. HINE and I. M. WARD, *J. Mater. Sci.* **28** (1993) 1107.
11. A. MEHTA and B. WUNDERLICH, *Coll. Polym. Sci.* **253** (1975) 193.
12. D. C. BASSETT and D. R. CARDER, *Phil. Mag.* **28** (1973) 513.
13. D. C. BASSETT, "Principles of Polymer Morphology", (Cambridge University Press, Cambridge 1981), Figs. 9.1 and 9.2.
14. M. YASUNIWA, K. HARAGUCHI, C. NAKAFUKU and S. HIRAKAWA, *Polymer J.* **17** (1985) 1209.
15. M. YASUNIWA, S. TSUBAKIHARA and C. NAKAFUKU, *ibid* **20** (1988) 1075.
16 D. C. BASSETT and B. TURNER, *Phil. Mag.* **29** (1974) 285.
17. D. C. BASSETT, B. A. KHALIFA and B. TURNER, *Nature* **239** (1972) 106.
18. A. S. MAXWELL, A. P. UNWIN and I. M. WARD, *Polymer* **37** (1996) 3293.
19. G. E. ATTENBURROW and D. C. BASSETT, *J. Mater. Sci.* **14** (1979) 2679.
20. A. S. MAXWELL, A. P. UNWIN and I. M. WARD, *Polymer* **37** (1996) 3283.
21. A. KELLER, M. HIKOSAKA, S. RASTOGI, P. J. BARHAM and G. GOLDBECK-WOOD, *J. Mater. Sci.* **29** (1994) 2579.
22. D. C. BASSETT, *Polymer* **17** (1976) 460.

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