

The mechanical behaviour of oriented high-pressure annealed polyethylene

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Four different grades of polyethylene have been annealed under high pressures, to transform the morphology, and then oriented by hydrostatic extrusion. The pre-extrusion morphology is shown to have a significant influence on the mechanical properties of the extrudates. At high crystallinities the mechanical behaviour of the extrudates can be interpreted using a simple aggregate model. This model suggests that high mechanical moduli can be obtained by orienting the crystallites more effectively and by increasing the crystallinity, which results in a higher shear modulus. However, the developments of crystallinity and lamellar size occur at the expense of reducing the integrity of the molecular network. Eventually this limits the efficiency of the orientation process and has a detrimental effect on the shear modulus and hence the extensional modulus of these oriented materials. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

This paper forms part of a series investigating the effects of pressure annealing and subsequent extrusion on the morphology and mechanical behaviour of different molecular weight grades of polyethylene. Other papers in the series show that high pressure annealing in the vicinity of the hexagonal phase produces considerable morphological changes, evident in increases in the crystallinity and crystal size¹, but that these occur at the expense of the integrity of the molecular network². These changes are most pronounced when annealing is performed within the intermediate phase, but it has been noted that, sometimes, annealing must be performed on the boundary between the orthorhombic and hexagonal phases if the subsequently extruded material is to have the maximum modulus. The optimum annealing position depends on factors such as the mean molecular length³ and the polydispersity with higher molecular weight grades yielding good mechanical behaviour when pre-annealed deeper within the hexagonal phase.

Here, the mechanical behaviour of oriented samples of pressure annealed polyethylene is interpreted using two theoretical models. The first, a simplified form of the single phase aggregate model, considers the sample to be an aggregate of oriented units of structure, with the extensional modulus of this aggregate dependent on the mechanical properties of the units and their orientation. The second model assumes that there are two mechanically independent phases, with the crystallites reinforcing a non-crystalline matrix, but accounts for the limiting reinforcing capacity of the crystallites in terms of their finite length. It is shown that the former model is appropriate when the crystallinity is high but that the latter model is more successful at lower crystallinity.

Together, these models are valuable in assessing the importance of the pre-extrusion morphology on the mechanical behaviour of the oriented material. They also provide an insight into the nature of the deformation mechanism.

EXPERIMENTAL

Four different molecular weight grades of high density polyethylene have been investigated; two high molecular weight (HD6007-EA and H02054P) and two ultra high molecular weight (R516 and GUR412) grades. *Table 1* contains details of these grades. High modulus oriented samples have been prepared from either the powder or pellet forms by a combination of melt extrusion or powder compaction, followed by pressure annealing in the vicinity of the hexagonal phase, to increase the lamellar thickness, and subsequent solid state extrusion. *Figure 1* illustrates schematically the location of the intermediate hexagonal phase in polyethylene and the route followed during annealing. A detailed description of the procedures used to prepare the samples is given elsewhere^{1,4} but the basic idea is to prepare samples with a range of morphologies and then extrude them to a fixed deformation ratio. The importance of the pre-extrusion morphology can then be assessed by studying the structure and mechanical properties of the extrudates.

Several distinct sets of samples of Grade A were produced to assess in turn the importance of the different annealing parameters, pressure, temperature and time. The annealing temperature and time were fixed at 234°C and 60 min respectively when preparing samples of the other grades; only the annealing pressure was altered. In this way samples with different pre-extrusion morphologies could be produced. Morphological characterization of these samples is reported elsewhere^{1,3} and confirms

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Table 1 High density polyethylene grades subjected to pressure annealing

Grade	Polymer	Source	Process	M_w	M_n
A	HD6007-EA	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	4 500 000	-

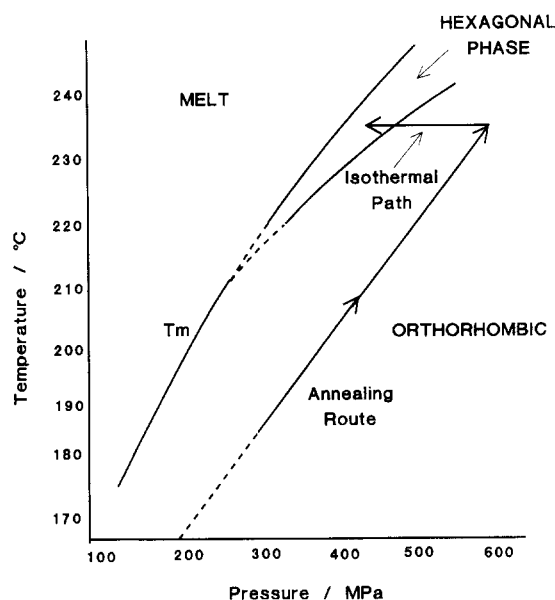


Figure 1 Schematic phase diagram for polyethylene and the path followed during high pressure annealing

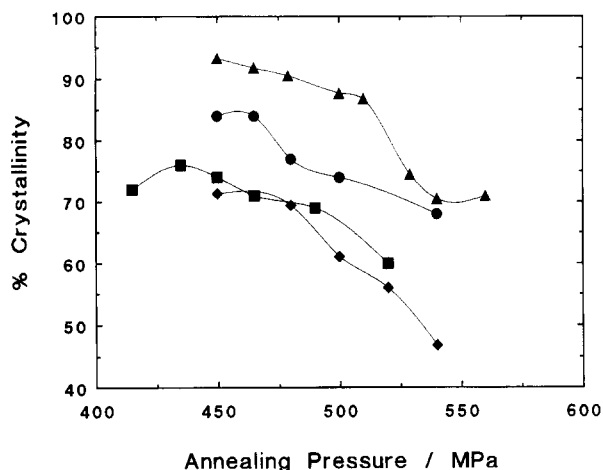


Figure 2 Variation in crystallinity as a function of annealing pressure. All samples annealed at 234°C and stated pressure for 1 h. ▲, Grade A; ●, Grade B; ■, Grade C; ◆, Grade D

substantial increases in both crystallinity and lamellar size as the annealing conditions approach and cross the orthorhombic-hexagonal border. For convenience the variation in crystallinity for each grade as a function of annealing pressure is reproduced in *Figure 2*.

The dynamic tensile and shear moduli of the extruded samples were determined in three point bend and torsion, respectively. In dynamic three point bend, samples were placed across two knife edge supports, 150 mm apart, and subjected to a sinusoidal driving strain imposed midway between the supports. An RMS displacement of

0.35 mm and a frequency of 1.7 Hz were used. Shear measurements were made on rods, approximately 120 mm long and between 2.5 and 1.8 mm in diameter, mounted vertically between the clamps of a torsion pendulum apparatus. The rods were set to oscillate by gently twisting the sample through an angle of approximately 6°, and thereafter the rotation of the sample was monitored using a photodyne to follow the light reflected from a mirror mounted on the upper clamp. The movement of the detector along the horizontal track was converted into an electrical signal and stored on computer. Values for the shear modulus were obtained from the time period of the oscillations and values for $\tan \delta$ from the decay in amplitude of successive oscillations.

Typical results for tensile and shear moduli, at temperatures between -150 and +75°C, are shown in *Figures 3* and *4* respectively. The data relate to samples of grade A annealed at different pressures, but extruded to the same deformation level, 7. Clearly, both moduli increase when the annealing pressure is reduced. A

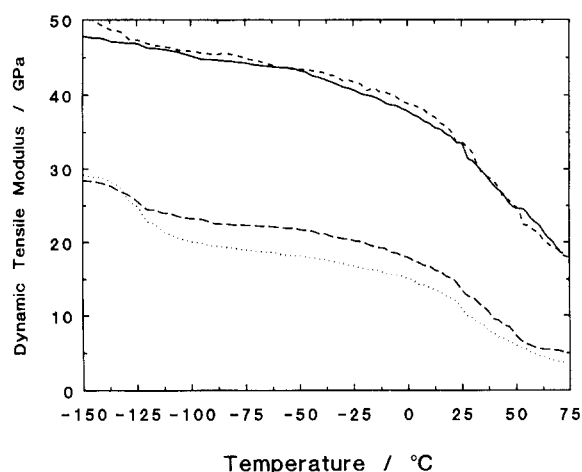


Figure 3 Tensile modulus of oriented samples of polyethylene, Grade A, as a function of temperature. All samples extruded to a deformation level of 7 after annealing at 234°C and stated pressure for 1 h. —, 480 MPa; ---, 500 MPa; - · - ·, 540 MPa; · · · ·, 585 MPa

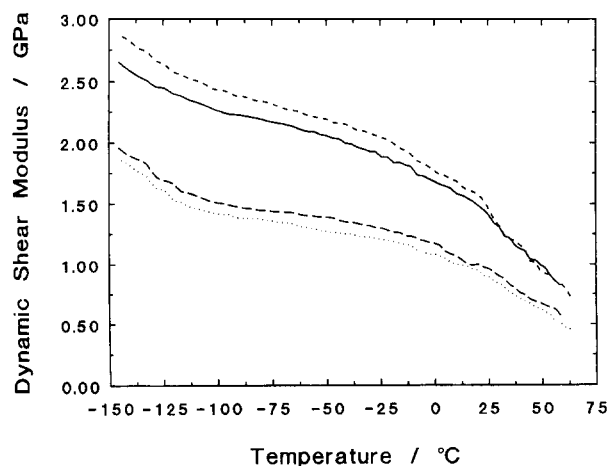


Figure 4 Shear modulus of oriented samples of polyethylene, Grade A, as a function of temperature. All samples extruded to a deformation level of 7 after annealing at 234°C and stated pressure for 1 h. —, 480 MPa; ---, 500 MPa; - · - ·, 540 MPa; · · · ·, 585 MPa

striking similarity in the general behaviour of both measures of modulus is also quite apparent. It is shown later that this behaviour is typical of a highly oriented single phase aggregate model. The effect of deformation level on the shear modulus of samples of Grade A with identical pre-extrusion morphology is shown in Figure 5. These data relate to the same temperature range as Figures 3 and 4 and show clearly that over this range the deformation process has no significant effect. Consequently, the variation in shear modulus shown in Figure 4 arises mainly from changes in the pre-extrusion morphology. This is important because an understanding of the factors which control the shear modulus is highly relevant to the later analysis using the aggregate model.

Wide angle X-ray scattering (WAXS) measurements were made on the 002 diffraction profile, to determine the crystallite orientation, and on the 200, 020 and 002 profiles to obtain the mean lamellar size. All measurements were made in transmission geometry on a Siemens Type T4 A605/1e two circle diffractometer using nickel

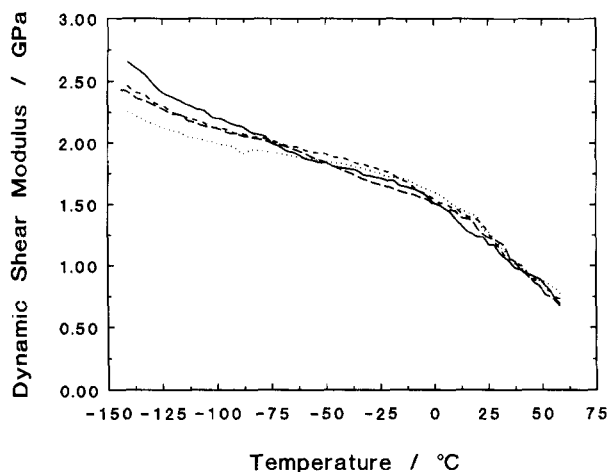


Figure 5 Shear modulus of oriented samples of polyethylene, Grade A, as a function of extrusion ratio. All samples annealed at 500 MPa and 234°C for 1 h before being extruded to a deformation ratio of: —, 5; ---, 7; - · - ·, 10; · · · ·, 14

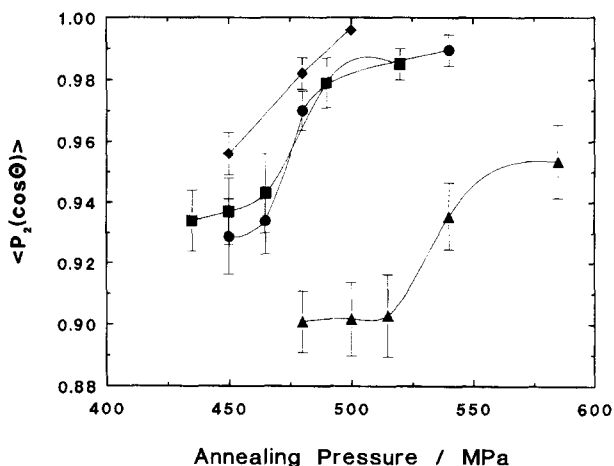


Figure 6 Crystalline orientation from WAXS as a function of annealing pressure. All samples extruded to a deformation level 7 after annealing at 234°C and stated pressure for 1 h. ▲, Grade A; ●, Grade B; ■, Grade C; ◆, Grade D

Table 2 Crystallite dimensions (Å) in pressure annealed polyethylene (grade D)

Pressure (MPa)	a-axis (2r) 200 Reflection	b-axis (2r) 020 Reflection	c-axis (L) 002 Reflection	Aspect ratio (L/r)
450	200	200	500	5.0 ± 0.6
480	190	180	290	3.1 ± 0.5
500	180	160	200	2.4 ± 0.4

Samples annealed at 234°C for 1 h and extruded to a ratio of $R_n = 7$

filtered copper K_α radiation. Orientational information was obtained by recording the diffracted X-ray intensity as a function of the angle between the scattering vector and the sample extrusion direction. Results in the form $\langle P_2(\cos\theta) \rangle$, the second moment averages, are shown in Figure 6 for the different grades. All samples have experienced the same macroscopic deformation, so for any grade, the crystallite orientation depends critically on the pre-extrusion morphology. Differences between the four grades may also relate to the different molecular weight distributions as well as the morphology. Generally, however, as the crystallinity is increased, by either decreasing the molecular weight or by reducing the annealing pressure, the crystallite orientation decreases.

The crystallite sizes, $\bar{L}_{(hkl)}$, were obtained from measurements of the breadth of the X-ray diffraction peaks, using the Scherrer equation:

$$\bar{L}_{(hkl)} = \frac{K\lambda}{b \cos\theta_{(hkl)}} \quad (1)$$

where b is the breadth of the diffraction profile, θ the Bragg angle, λ the wavelength and K a constant, assumed to be unity here. High resolution 2θ scans were used to obtain the experimental diffraction profiles and these corrected for instrumental broadening. Table 2 gives results for the crystallite sizes along the a, b and c axes in pressure annealed samples of Grade D. The predominant change, along the c axis, leads to an increase in the aspect ratio as the annealing pressure is reduced. Crystallite size measurements on the other grades are not relevant to the analysis presented later. Nevertheless, it can be concluded that generally, development along the c-axis is more pronounced in the lower molecular weight grades and often beyond the resolution of our apparatus (>100 nm) especially when annealing is performed well within the hexagonal phase.

MECHANICAL MODELLING

Aggregate model

The mechanical behaviour of several highly oriented materials has been interpreted successfully using a simplified aggregate model^{5,6}. The similarity in the behaviours of the tensile and shear moduli is the clue that the model may also be applicable here. In essence, the model⁷ assumes that the sample is composed of an aggregate of identical anisotropic units, and that the macroscopic properties of the sample can be obtained by averaging the individual contributions from each unit, which depend on the orientation. This averaging procedure can be applied to either the compliance constants (Reuss averaging), assuming uniform stress, or the stiffness constants (Voigt averaging), assuming

uniform strain. In the present study Reuss averaging is used, as this generally gives better agreement with experiment.

For high orientation the Reuss form of the aggregate model simplifies to the following relation⁵ between the tensile, E , and shear, G , moduli of the sample.

$$\frac{1}{E} = \frac{1}{G} \langle \sin^2 \theta \rangle + \frac{1}{E_u} \quad (2)$$

where θ is the angle between the longitudinal direction of the aggregate unit and the extrusion direction in the sample and E_u is the tensile modulus of the aggregate unit. Consequently, a plot of values of $1/E$ against $1/G$ obtained over a range of temperatures, should give a straight line with gradient and intercept related to the orientation and properties of the unit.

Figures 7–9 generally show that the model can be applied successfully to oriented samples of grade A which have been subjected to a wide range of processing conditions. Figure 7 considers samples which have all undergone the same macroscopic deformation, but which have been subjected to different annealing pressures in the range 585–480 MPa before extrusion.

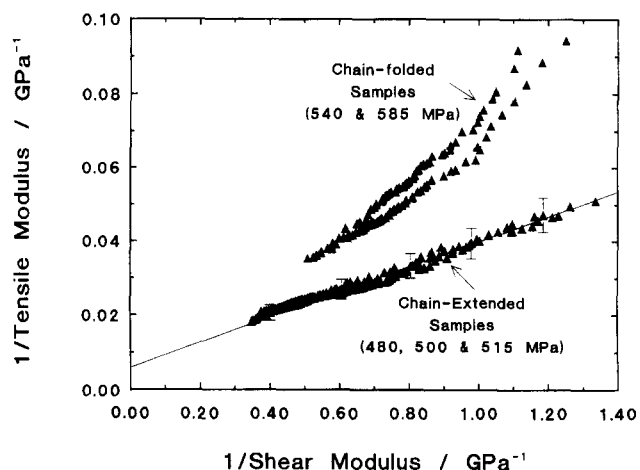


Figure 7 Application of aggregate model to oriented samples of polyethylene, Grade A. All samples extruded to a deformation level 7 after annealing at 234°C and stated pressure for 1 h

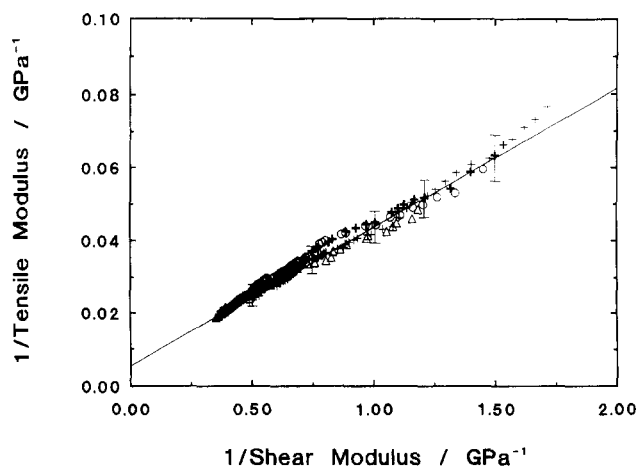


Figure 8 Application of aggregate model to oriented samples of polyethylene, Grade A. All samples extruded to a deformation level 7 after annealing at 500 MPa and stated temperature for 1 h. 232°C, +; 234°C, Δ; 236°C, ○; 238°C, +

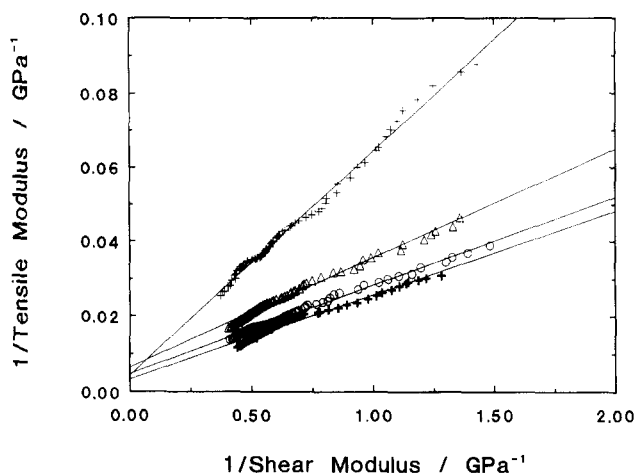


Figure 9 Application of aggregate model to oriented samples of polyethylene, Grade A. All samples annealed at 500 MPa and 234°C for 1 h before being extruded to a deformation level of +, 5; Δ, 7; ○, 10, and +, 14

Table 3 Aggregate model parameters for samples of Grade A

Annealing parameter	$\langle \sin^2 \theta \rangle$	E_u (GPa)
Pressure (480–515 MPa)	0.033	170
Temperature (232–238°C)	0.036	180
Time (5–300 min)	0.031	180
Extrusion ratio		
$R_n = 5$	0.061	220
$R_n = 7$	0.033	170
$R_n = 10$	0.024	210
$R_n = 14$	0.022	240

The experimental error is ± 0.003 in $\langle \sin^2 \theta \rangle$ and ± 30 GPa in E_u

There are two distinct regions. Good agreement with the model is shown for pressures between 480 and 515 MPa. It is shown elsewhere¹ that such samples have a pre-extrusion morphology characteristic of annealing either within or on the boundary of the hexagonal phase. It is also noticeable that, to a first approximation, the data for samples annealed in this region lie on a common line. Values for the unit orientation and modulus, obtained from the gradient and intercept, in this region are given in Table 3. The model is not successful, however, in samples annealed at pressures greater than 515 MPa. These samples do not undergo such drastic morphological changes during annealing, but essentially retain the typical chain-folded morphology and have a low crystallinity.

The general trends observed above when using pressure to alter the morphology are confirmed when temperature is used as the annealing variable (Figure 8). Again, although individual samples have different mechanical properties, the data all lie on a common line and yield similar values for the model parameters found above (Table 3). Evidence of poorer agreement with the model is apparent for an annealing temperature of 232°C, where a slight upward curvature is seen at the low modulus end. Table 3 also lists the parameter values obtained when time is used as the annealing variable. Deviation from the model was only shown by the sample annealed for 5 min and even this only became apparent at high temperatures (i.e. low modulus), in a manner similar to that shown by the 232°C sample in Figure 8.

These discrepancies relate to the pre-extrusion morphology which is still predominately chain-folded in these samples.

The influence of the extrusion ratio is assessed on samples of a fixed pre-extrusion morphology in Figure 9. Each sample produces a reasonable straight line fit, with all the lines intercepting the y-axis at approximately the same position (Table 3). Furthermore, the gradient decreases as the extrusion ratio is increased, indicating, as expected, that the degree of orientation increases with the extrusion ratio.

The mechanical behaviour of the three remaining grades has also been analysed using the simplified aggregate model, although only the effects of altering the annealing pressure, to change the pre-extrusion morphology, have been considered. In the case of grades B and C the behaviour is very similar to that observed for Grade A in Figure 7, with samples annealed at lower pressures showing reasonable agreement with the model. The results are presented in Table 4 and the differences between these grades illustrated in Figure 10. A slight problem arises in the case of Grade C. Data relating to samples of this grade, annealed at different pressures, show a relatively common linear relation between $1/E$ and $1/G$. However, there is a spread in the values of the y-axis intercept and this is reflected in Table 4. This variation in the intercept implies that the tensile modulus for the aggregate unit changes with changes in morphology. In Grade D the anomalies are more serious and agreement with the model is not found. Figure 11 shows that the graphs are not linear and that extrapolation of the curves at high modulus results in a negative y-axis intercept.

Table 4 Aggregate model parameters for different grades of polyethylene

Grade	$\langle \sin^2 \theta \rangle$	E_u (GPa)
A	0.033	170
B	0.024	200
C	0.040	120–260

The experimental error is ± 0.003 in $\langle \sin^2 \theta \rangle$ and ± 30 GPa in E_u

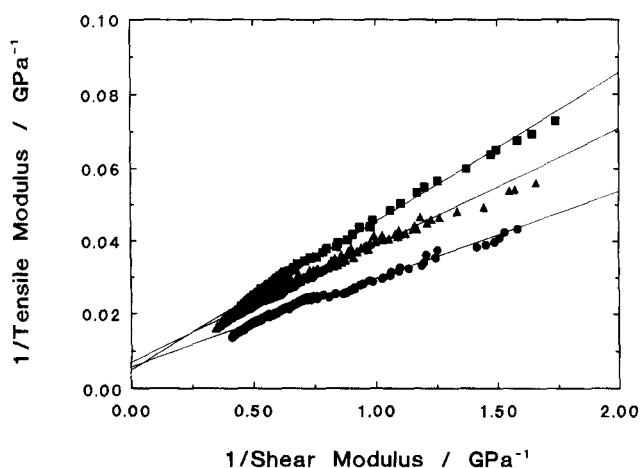


Figure 10 Application of aggregate model to oriented samples of polyethylene. All samples annealed at 500 MPa and 234°C for 1 h before being extruded to a deformation level of 7. \blacktriangle , Grade A; \bullet , Grade B; \blacksquare , Grade C

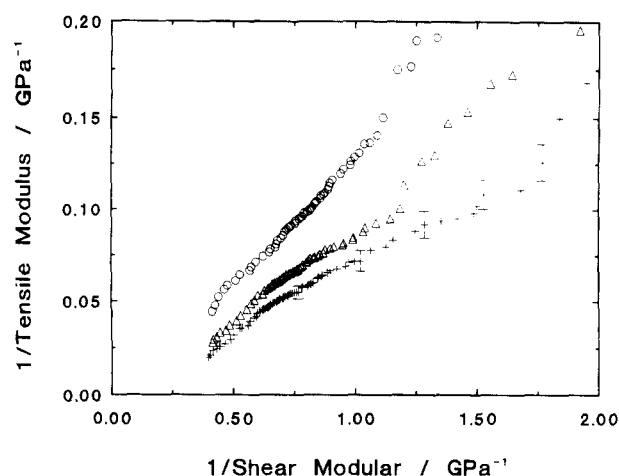


Figure 11 Application of aggregate model to oriented samples of ultra high molecular weight polyethylene, Grade D. All samples extruded to a deformation level 7 after annealing at 234°C and stated pressure for 1 h. $+$, 450 MPa; Δ , 480 MPa; \circ , 500 MPa

The general conclusion that can be derived from the above results is that the aggregate model is successful when applied to samples which have been annealed within or on the boundary of the high pressure hexagonal phase for a time sufficiently long to allow the development of both the high crystallinity and the enhanced crystal size. Those samples which have been annealed away from the phase boundary or which have not developed the appropriate morphology, either because of entanglement restrictions or insufficient time, show a distinct upward curvature at high temperatures (low modulus). This type of failure is attributed to the relatively low crystallinity of these samples and is less extreme at the lower temperatures where there is little distinction between the crystalline and non-crystalline phases. At higher temperatures the mechanical properties of the two phases differ considerably and it is not unreasonable that a simple single phase model should fail. Indeed, as will be shown now, a model based on two phases is more successful in the UHMWPE Grade D which shows relatively low crystallinity even in samples annealed within the hexagonal phase.

Fibre composite model

The breakdown of the single phase aggregate model in the high molecular weight samples, presumably because of the existence of two distinct phases, justifies the use of a more appropriate model. One of the simplest two phase models involves the series arrangement of the phases such that both phases experience the same stress. In this case the macroscopic properties are obtained by averaging the compliances. A more sophisticated two phase model is the short fibre composite model⁸⁻¹¹ which considers the sample as a composite of short needle-like lamellae embedded in an amorphous matrix. The model accounts for the reduced load bearing capacity of the fibres because of their finite length using a parameter known as the shear lag factor, Φ , which depends strongly on the fibre aspect ratio and the shear modulus. For a parallel arrangement of the phases, the modulus of the polymer E_p , is given by

$$E_p = E_f V_f \Phi + (1 - V_f) E_a \quad (3)$$

with

$$\Phi = \left[1 - \frac{\tanh B}{B} \right]$$

where

$$B = \left[\frac{l_f}{r_f} \right] \left[\frac{G_m}{E_f \ln(\pi/2\sqrt{3}V_f)} \right]^{1/2}$$

and l_f , r_f , E_f and V_f are the fibre length, radius, tensile modulus and volume fraction respectively, and G_m is the shear modulus of the matrix.

Predictions of mechanical behaviour using the two phase models require a knowledge of the mechanical properties of the individual phases. The modulus of the crystalline phase E_c , is assumed to be 255 GPa, as obtained by Clements *et al.*¹² using X-ray analysis. It is not possible to obtain the modulus of the amorphous phase E_a directly from mechanical measurements but its value has been estimated from the shear modulus using the equation $E = 2G(1 + \nu)$, valid for an isotropic medium¹³, and assuming that Poisson's ratio $\nu = \frac{1}{2}$. Finally the relative phase concentrations were obtained from differential scanning calorimetry¹.

Figure 12 compares experimental measurements of tensile modulus with those predicted by a simple series model for the highest molecular weight material, Grade D. Although the series model does not fit the experimental data particularly well, the fit is much better than a parallel model would provide and it does predict the general trend with temperature. As the crystallinity is increased, by annealing at lower pressures, the modulus at any temperature also increases and the discrepancy between experiment and prediction becomes more noticeable.

A much better fit is obtained if the short fibre composite model is used. In this analysis values for the tensile modulus and volume fraction of the crystalline phase are the same as those used above. The shear modulus is taken directly from data in Figure 5. The remaining parameter, the aspect ratio of the lamellae, is unknown but a value for it is obtained by fitting to the low temperature (-50°C) modulus. This value has then

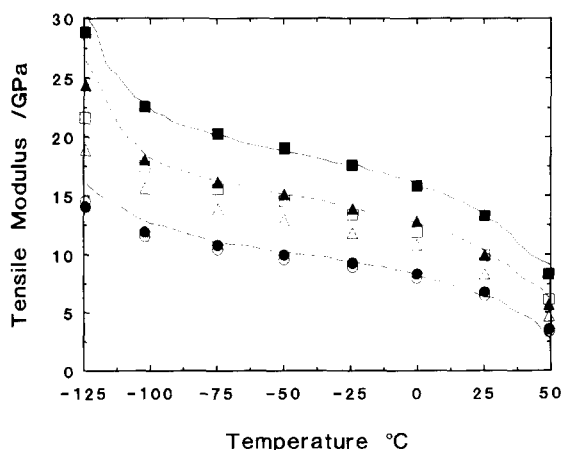


Figure 12 Comparison of experimental and predicted tensile modulus of oriented polyethylene, Grade D. Experimental values: —, 450 MPa; - - -, 480 MPa; - - -, 500 MPa. Predicted values: ■, 450 MPa; ▲, 480 MPa; ●, 500 MPa. Open symbols – simple series model and filled symbols – fibre composite model

Table 5 Values for the crystallite aspect ratios in pressure annealed polyethylene

Annealing pressure (MPa)	450	480	500
WAXS	5.0	3.1	2.4
Cox model	3.75	3.60	3.45

Samples of Grade D annealed at 234°C for 1 h and extruded to a ratio of 7

been used to model the temperature dependence of the modulus and the results are also shown in Figure 12. The aspect ratio values determined in this way are listed in Table 5 where it can be seen that they are similar in magnitude to those obtained from WAXS. The results are not exactly equivalent, but this is perhaps not too surprising considering the large uncertainty in the WAXS results and the assumptions involved in the composite model. The important conclusion is that the increase in modulus, observed in extrudates whose pre-extrusion morphology has been altered, is more reasonably explained by increases in crystallite aspect ratio than it is by increases in the crystallinity alone.

DISCUSSION

Electron microscopy studies on these samples¹ show that the morphological changes produced by pressure annealing isotropic polyethylene depend critically on the molecular weight distribution and the specific annealing conditions. Generally, changes are most pronounced when annealing is performed in the region of the orthorhombic hexagonal phase boundary, the position of which is dependent on the molecular weight^{14,15} and the lamellar size¹⁶. (With reference to Figure 1, high molecular weight and lamellar size both result in a shift of the hexagonal orthorhombic phase boundary to lower pressure or higher temperature.) The results reported here show that pressure annealing also has a significant influence on the mechanical behaviour of the subsequently oriented material and the aim of this work is to understand this influence in terms of the previously discussed morphological changes. To facilitate this approach the majority of the work concentrates on samples deformed to the same macroscopic level, so that differences in the mechanical properties can be correlated to morphological changes in the isotropic material produced by pressure annealing.

Surprisingly, although the samples investigated here cover a wide range of molecular weight distributions and morphologies, two relatively simple models adequately describe the main features of the mechanical behaviour. At the high crystallinities, achievable in the medium molecular weight Grades A and B, the simplified aggregate model is very successful. This model begins to show some evidence of breakdown in less highly crystalline samples of these grades, where annealing conditions have prevented the bulk of the sample from entering the hexagonal phase, as well as in samples of Grade C, where the higher molecular weight and entanglement density have restricted the development of crystallinity even in samples annealed within the hexagonal phase. This breakdown of the model is apparent in changes in the y-axis intercept (unit

modulus) and in the deviation from linearity at high temperatures. In the highest molecular weight grade, D, where the crystallinity remains low for all annealing conditions examined, a fibre composite model recognizing the two phase nature of the material is more successful. The mechanical improvement in these samples arises from the more effective reinforcement imparted by crystallites with higher aspect ratios. Interestingly, both models are critically dependent on the shear modulus.

The extensional modulus of the fundamental unit in the aggregate model, obtained from the y-axis intercept of plots such as *Figure 7*, has a relatively constant value of about 200 GPa (*Table 3*) for the wide range of samples investigated. This compares with an early estimate of 180 GPa for the modulus of the polyethylene crystal¹⁷, but more recent work¹⁸ suggests a higher value, possibly as high as 330 GPa¹⁹. This correspondence suggests that the aggregate unit may well be a microaggregate of crystals. Small quantities of non-crystalline material within such aggregates would explain the lower modulus of the aggregate unit. This interpretation of the aggregate unit is also supported by the good correspondence between the orientation of the aggregate units and that of the crystallites (*Tables 6 and 7*). Differences between the two values, particularly for Grades A and B, are generally within experimental error, but it is noticeable that the WAXS values are systematically lower. This is perhaps indicative of a spread of crystallite orientations within the aggregate. In the higher molecular weight Grades C and D there is a growing discrepancy between these values, but this is attributable to the drop in crystallinity in these materials and the breakdown of the aggregate model.

The success of the aggregate model provides the means for investigating the factors leading to improved mechanical behaviour. Equation (2) essentially shows that the macroscopic extensional compliance is dominated by a shear term which depends on the intrinsic shear modulus and the orientation of the units which comprise the sample. To identify exactly what is happening it is therefore necessary to investigate the behaviour of both these parameters separately. *Figure 5* shows that, to a first approximation, the shear modulus

Table 6 Orientation moment averages, $\langle P_2(\cos\theta) \rangle$, for extruded samples of Grade A

Extrusion ratio	WAXS	Aggregate model
5	0.85 ± 0.02	0.86 ± 0.03
7	0.90 ± 0.02	0.92 ± 0.03
10	0.91 ± 0.02	0.94 ± 0.03
14	0.92 ± 0.02	0.95 ± 0.03

All samples annealed at 500 MPa, 234°C for 1 h

Table 7 Orientation averages, $\langle P_2(\cos\theta) \rangle$, for different molecular weight grades

Polymer grade	WAXS	Aggregate model
A	0.90 ± 0.02	0.92 ± 0.03
B	0.92 ± 0.02	0.94 ± 0.02
C	0.94 ± 0.01	0.91 ± 0.03
D	0.96 ± 0.01	0.84 ± 0.04

Chain-extended samples that have been extruded to a ratio of 7

is unaffected by the deformation level, whereas *Table 3* and *Figure 9* show that the unit orientation does improve. Clearly, then, extrusion is simply a means of orienting the crystallites, with higher levels of deformation producing better orientation and the mechanical improvement is interpretable solely on this basis.

To consider the effects of pre-extrusion morphology on mechanical behaviour it is useful first to examine samples of Grade A which have undergone identical macroscopic deformations but different initial annealing treatments. *Table 3* and *Figures 7 and 8* show that, to a first approximation, the orientation of the units is independent of the annealing conditions, $\langle \sin^2\theta \rangle$ remaining about 0.033 ± 0.003 . It has already been shown that the extensional modulus of the unit is also unaffected by the annealing, so it follows from equation (2) that changes in the extensional modulus must arise from changes in the shear modulus. As shown above, the deformation level does not affect the shear modulus so it appears that the shear modulus of the oriented sample is determined by the pre-extrusion morphology produced by pressure annealing.

Figure 13 shows how changes in the annealing pressure affect the shear modulus of the different grades examined here. All four grades show an increase in the shear modulus when annealed closer to the intermediate phase. The basic factor controlling the shear modulus is the increasing crystallinity which follows from lower pressure annealing. The upturn in shear modulus for all four grades corresponds to the upturn in crystallinity shown in *Figure 2*. However, it is not controlled by the crystallinity alone because a plot of crystallinity versus shear modulus for all samples is not unique. This is obvious because the drop in the shear modulus of Grade A at low annealing pressure occurs despite a continuing increase in the crystallinity. This fall is attributed to the decreasing effectiveness of the network which links different crystallites. As a consequence inter-crystalline shear begins to override the beneficial effect of increasing crystallinity and introduces a significant contribution to the macroscopic compliance and hence a drop in both the shear and tensile moduli.

Figure 13 also shows that Grade A displays the highest shear modulus over the range of annealing conditions shown. This might imply that Grade A should also show

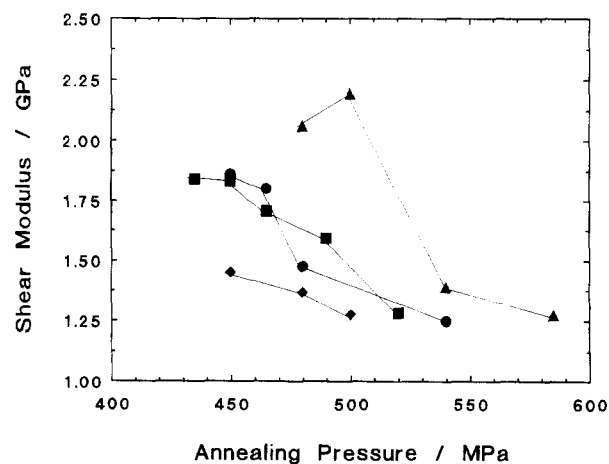


Figure 13 Variation in room temperature shear modulus with annealing pressure. All samples annealed at 234°C and stated pressure for 1 h. ▲, Grade A; ●, Grade B; ■, Grade C; ◆, Grade D

the highest extensional modulus but in fact this is shown by Grade B. The explanation hinges on the higher orientation achieved in this grade, as is shown in *Figure 10*. A lower $\langle \sin^2 \theta \rangle$ term has the effect of reducing the total shear term in equation (2) and consequently the tensile modulus is greater even though the shear modulus of Grade B is less than that of Grade A. Obviously the better orientation of the units in Grade B is the important factor.

The development of crystallite orientation with extension ratio is quite complex. The dominant factor appears to be the level of crystallinity. *Table 7* shows that orientation is higher in the low crystallinity high molecular weight grades and *Figure 6* confirms this trend with the level of orientation dropping in the more highly crystalline samples. *Figure 14* shows the development of crystalline orientation (and because of the good agreement in *Table 6* the aggregate units) with extrusion ratio in typical highly crystalline samples. The solid line, describing a pseudo-affine deformation, that is the orientation of needles in a matrix, clearly gives good agreement with experiment and provides a clue to the nature of the deformation process. The common gradient in *Figures 7* and *8* suggests that most of the highly crystalline samples orient in a similar way, although there are some small differences; viz. Grade A has a slightly higher orientation than Grade B. These differences may relate to the nature of the molecular network which is also altered by the pre-extrusion annealing process with the developments in crystallinity occurring at the expense of the integrity of the molecular network². The overdestruction of the network in the annealing process is presented in the accompanying paper² as the explanation for the poor orientational development reported by Chuah *et al.*²⁰. There may also be other influences, such as the level of crystallinity and crystallite aspect ratio, which oppose the orienting tendency of the network and hence introduce complications. A further complication may arise from changes in the crystalline amorphous interphase which accompany annealing.

Although the simple series model gives a relatively good prediction of the modulus/temperature behaviour

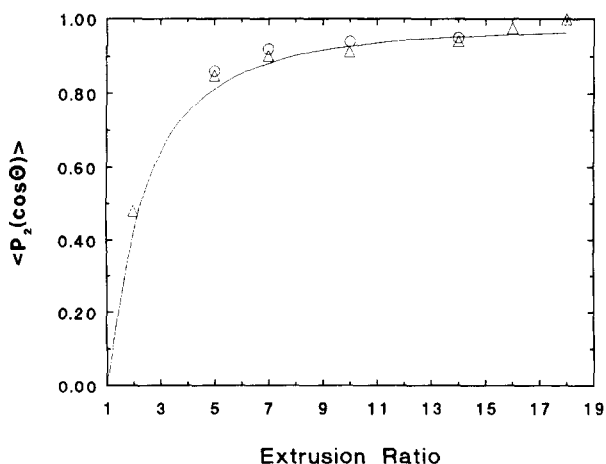


Figure 14 The development of crystallite orientation with extrusion ratio for highly crystalline anabarically annealed polyethylene. Δ , From WAXS and \circ , aggregate model analysis. The solid line represents pseudo-affine deformation

in the low crystallinity material, the increase in crystallinity resulting from pressure annealing yields a greater improvement in the mechanical properties than is expected from this model. A greater reinforcement can be provided by changes in the mechanical coupling resulting from the formation of crystalline bridges¹¹ between the lamellae but it is unlikely that these will have formed at such low deformation ratios. A better explanation centres on the reinforcing nature of the crystallites and a simple composite model analysis shows that the required increase in the aspect ratio of the crystal is in line with the changes measured in WAXS and is consistent with the lamellar growth which is known to accompany annealing within the hexagonal phase.

CONCLUSIONS

The mechanical behaviour of a series of extruded pressure annealed polyethylenes has been examined in detail to ascertain the importance of morphological changes induced by annealing within the hexagonal phase. Basically, the annealing process produces highly crystalline samples with high aspect ratios at the expense of the integrity of the molecular network. During deformation the crystallites are effectively oriented by the network provided it retains sufficient integrity, although it appears that the physical impingement of the crystallites upon one another acts to oppose this influence. Consequently the high molecular weight grades, with low crystallinity and high entanglement density orient most efficiently. The efficient development of orientation is not, however, accompanied by an efficient development of the macroscopic tensile modulus. This is attributed to the retention of the highly compliant non crystalline phase. The relatively successful modelling of the ultra high molecular weight material using a two phase fibre composite model confirms that one way of improving the modulus is to use pressure annealing deep within the hexagonal phase as a way of increasing the aspect ratio and hence the reinforcing effectiveness of the crystallites.

This approach does not extend to the lower molecular weight materials where annealing within the hexagonal phase leads to a reduction in the effectiveness of the molecular network. This is apparent in the detrimental effect on the shear modulus when inter-crystalline shear predominates. The consequence of this on the macroscopic tensile modulus is understood using a simplified aggregate model. The best way to improve the tensile modulus centres on reducing the shear compliance term by improving either the orientation or the shear modulus. The shear modulus is determined by the morphology produced by pressure annealing with higher crystallinities producing better shear moduli, but the development of the crystallinity must not occur at the expense of the network integrity. This balancing act between crystalline development and network retention is sensitive to molecular weight and polydispersity, so that the specific annealing conditions required to optimize the mechanical properties vary from grade to grade. In the low molecular weight material it is important to prevent the material fully entering the hexagonal phase.

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