

The effect of high pressure annealing on the molecular network in polyethylene

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The changes in the molecular network of several grades of polyethylene subjected to high pressure annealing are followed using a simple model which combines thermal expansion and mechanical measurements. It is found that annealing reduces the degree of molecular entanglement, particularly when performed well within the intermediate hexagonal phase. It is shown that this process can be used to improve the drawability and hence the ultimate physical properties of high molecular weight material. In low molecular weight material it is necessary to retain a sufficiently intact network which can orient the crystallites effectively and which prevents the material from becoming friable. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The high pressure (anabaric) annealing of polyethylene within its intermediate phase is known to produce considerable changes in the morphology^{1–3}. Most obvious are the large increases in both lamellar size and crystallinity, and it is these particular benefits which have led to the use of this process, coupled with subsequent orientation, in attempts to produce high modulus material^{4–7}. The success in this field, however, has been limited, with early attempts^{4,5} yielding samples with very poor properties. Other efforts^{6,7} were more successful with values as high as 50 GPa being reported for the macroscopic modulus of some samples. A common conclusion^{5,7} of these early efforts is the suggestion that the obvious morphological changes produced by annealing are also accompanied by changes in the molecular network which are critical in determining the success of the technique.

The role played by the molecular network in determining the drawability of a polymer has underpinned explanations of the differences between melt-spun and gel-spun material^{8–10}. This work has led to the widely held belief that optimum drawing requires a balance between two conflicting needs. First, it is known that the molecular network is an essential element for the development of crystalline orientation⁸ and it is therefore necessary to have a sufficiently intact network that can orient the crystallites effectively. At the same time, the preservation of the network during drawing, as is indicated by recent neutron scattering studies¹¹, implies that it must not be so restrictive that it limits the drawability and hence the ultimate physical properties of the material. An additional concern is the probable deleterious effect that an excessive unravelling of the molecular network might have on the material strength.

The possibility that pressure annealing may provide a means of modifying the network to achieve an optimum balance between these conflicting requirements is clearly of interest.

The parameter which characterizes the molecular network in non-crosslinked polymers, is the density of semi-permanent junction points. The two main sources of these junction points are the physical entanglements, present in the amorphous regions, and the crystallites, with the proportion arising from each of these sources varying according to the polymer grade and morphology. It is not easy to obtain direct information on this parameter, but generally the network has been investigated by means of shrinkage force measurements¹², although more recently, stress-strain curve matching¹³ has been used. In dimensionally large highly crystalline samples these techniques are not appropriate and so an alternative means must be found.

A possible solution to this problem is presented by a model proposed by Orchard *et al.*¹⁴ to explain the observation that the negative thermal expansion coefficient of some highly oriented polyethylene samples is greater than that of the isolated crystal. This additional retraction is attributed to the entropic retractive force of the molecular network, and the model relates changes in the thermal expansion with temperature to parallel changes in the network stress and the sample stiffness. Thus, measurements of thermal expansion and modulus can in effect be used to probe the molecular network.

This paper is one in a series examining in detail the effects of high pressure annealing (in particular the role played by the hexagonal phase) on different molecular weight polyethylenes. The changes in morphology produced by the annealing process and the implications for achieving high modulus are reported in greater detail elsewhere. Here, however, attention focuses on the molecular network, which is characterized using the

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model proposed by Orchard *et al.*¹⁴. By concentrating on samples which have all been drawn to the same extent, but which have undergone different annealing histories, changes in the network produced by pressure annealing have been identified. These changes have been correlated with changes in the mechanical properties to illustrate the critical role played by the molecular network.

EXPERIMENTAL

Four different grades of high density linear polyethylene, details of which are given in *Table 1*, have been investigated. In the case of Grade A, billets were prepared using starting material in pellet form, but difficulties associated with melt-processing higher molecular weight material meant that billets of these grades were prepared by powder compaction. Rod shaped samples were machined from these billets and then pressure annealed, either within the hexagonal phase or in its vicinity on the border with the orthorhombic phase, in a purpose built vessel, described elsewhere⁷. *Figure 1* shows schematically the location of the intermediate hexagonal phase in polyethylene and the route followed during annealing. Distinct sets of annealing conditions were chosen so the effects of pressure, temperature and time could all be considered separately. After annealing, the samples were extruded at 100°C and a speed of 5 mm min⁻¹ to a fixed deformation ratio of 7, although in the case of grade A, samples covering a range of deformation ratios were also prepared to test the applicability of the network model.

Dynamic mechanical and thermal expansion measurements were made on the extruded samples over a range of temperatures. The dynamic bending modulus was measured in three point bend on samples of aspect ratio greater than 40 at a frequency of 1 Hz. Measurements of the axial thermal expansion coefficient, α , were made on sections of extrudate 6 mm long, with the ends ground square, on equipment built in-house¹⁴. Temperature and length changes were recorded simultaneously on a XY plotter. Temperature ramping in both positive and negative directions at a rate of 1.5°C min⁻¹ was employed to minimize the effects of thermal lag. The experimental error in α is estimated at $\pm 0.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

Measurements of crystalline orientation were made on a Siemens two circle diffractometer using nickel filtered copper K_α radiation. Calculations of the Legendre moment averages of the orientation distribution function were made from intensities corrected for volume illumination and absorption, and assuming transverse isotropy.

RESULTS

Deformation behaviour

Most samples extruded to a deformation level of 7 successfully, although problems were encountered in two respects. The first, concerning lower molecular weight material, can be illustrated by reference to *Figure 2* where the extrusion pressure is plotted against extrusion rate for samples of Grade A. As the morphology is altered, by reducing the annealing pressure and hence taking the sample further into the hexagonal phase, the pressure required to extrude at a specific rate increases initially before dropping suddenly for samples annealed below 480 MPa. This drop in extrusion pressure coincides with the onset of pronounced cracking of the extrudate. Such samples are termed incoherent, tending to break if dropped, and often breaking up during extrusion. Samples of Grade B also suffered from this problem if the annealing pressure was too low.

The very high molecular weight material showed a different sort of problem. Powder compacted samples of Grade D could not be extruded to a deformation ratio of 7 unless they were annealed beforehand. Pressure annealing is therefore shown to impart an enhanced drawability to very high molecular weight material. These contrasting results strongly suggest the existence of optimum annealing conditions, and this is supported further by the mechanical measurements presented later.

Dynamic modulus

Figure 3 illustrates the variation in the dynamic modulus over the temperature range -150 to +70°C for samples of Grade A extruded to different deformation ratios. All samples show the expected fall in modulus as the temperature is increased. At about -100°C this drop in modulus is relatively insensitive to temperature changes, but at about room temperature it becomes much more pronounced. As expected, the modulus at a fixed temperature is found to increase with deformation ratio although surprisingly, as is shown elsewhere¹⁵, the development is very close to that expected for pseudo-affine deformation.

Figure 4 shows the variation in the modulus of samples of identical nominal deformation ratio but different pre-extrusion morphology produced by altering the annealing pressure. Evidence of an optimum annealing pressure, in terms of the final modulus, is clearly shown by three grades, the exception being Grade D where the curve suggests that the optimum pressure occurs at a value below the range investigated. This is consistent with the observed general trend for the optimum annealing pressure to move to lower values, equivalent to deeper penetration into the hexagonal phase, as the molecular weight is increased. The effects of altering the

Table 1 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	-

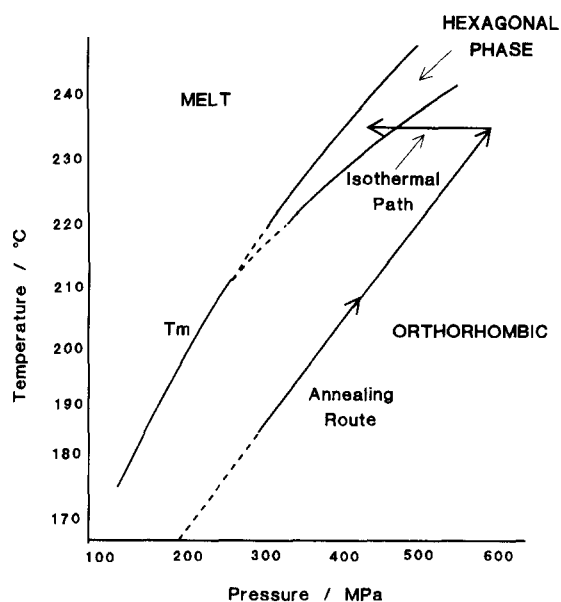


Figure 1 Schematic phase diagram for polyethylene and the path followed during high pressure annealing

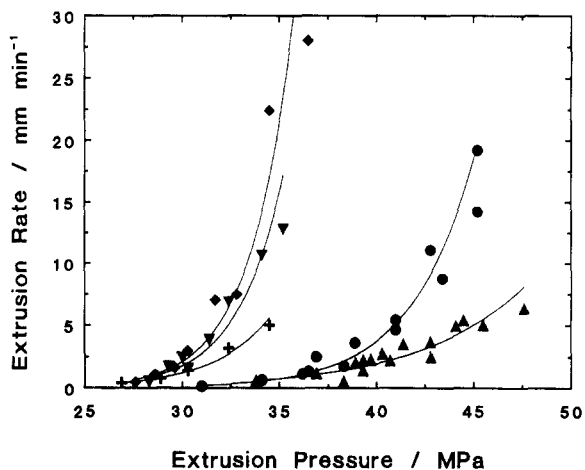


Figure 2 The extrusion pressure of annealed polyethylene (Grade A) as a function of extrusion rate. Samples annealed at 234°C for 1 h at the pressure indicated; +, 450; ▲, 480; ●, 515; ▼, 545; ◆, 580 MPa

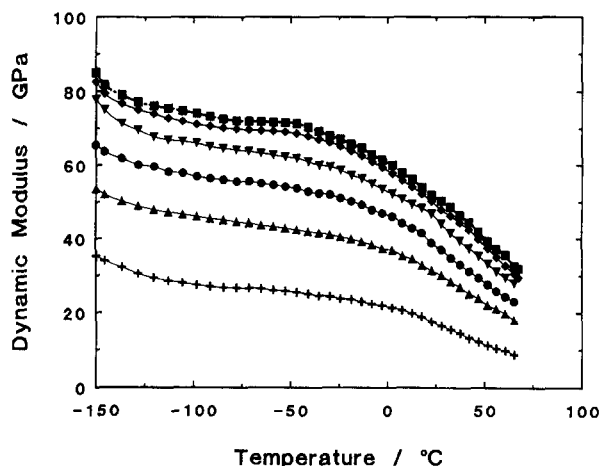


Figure 3 The dynamic modulus of pressure annealed polyethylene (Grade A) as a function of temperature. Samples annealed at 500 MPa and 234°C for 1 h and then extruded to deformation level; +, 5; ▲, 7; ●, 10; ▼, 14; ◆, 16; ■, 18

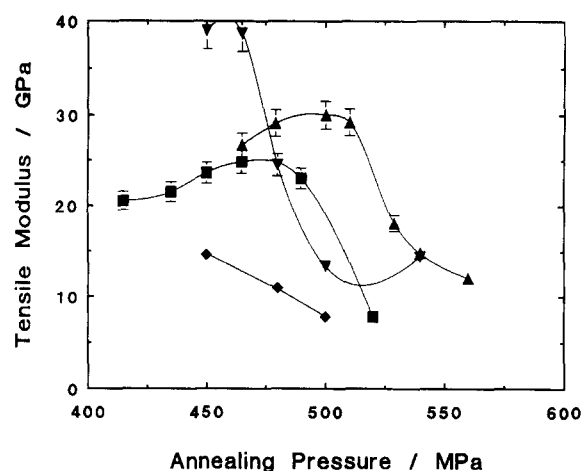


Figure 4 The tensile modulus of different molecular weight polyethylenes as a function of annealing pressure. All samples extruded to deformation level 7 after annealing for 1 h at 234°C and the pressure shown. ▲, Grade A; ▼, Grade B; ■, Grade C; ◆, Grade D

other annealing parameters have only been examined in Grade A but these results support the existence of sets of optimum annealing conditions.

Thermal expansion

Some typical thermal expansion results obtained in the temperature range -20°C to $+10^{\circ}\text{C}$ are shown in Figure 5. As was the case in Figure 3 these relate to extrudates of Grade A with different levels of deformation, but similar pre-extrusion morphologies. All samples show a very large negative thermal expansion, which becomes more negative as temperature increases. Values as highly negative as $-16 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, considerably greater in magnitude than the intrinsic crystal thermal expansion¹⁶, ($-12 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$), are shown by some samples. Similar behaviour prompted Orchard *et al.*¹⁴ to an explanation based on an entropically driven stress.

THE NETWORK MODEL

The network model¹⁴ was originally developed to explain the large negative thermal expansion coefficients observed in highly oriented polyethylene films. The applicability of

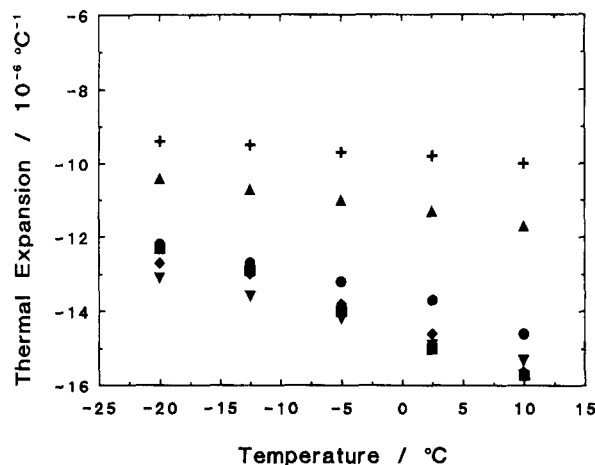


Figure 5 The longitudinal thermal expansion of pressure annealed polyethylene (Grade A) as a function of temperature. See Figure 3 for key to samples

the model to these pressure annealed samples will first be tested, before it is used as a probe to investigate the effects of annealing on the molecular network.

In essence, the model assumes that the polymer is composed of two main components, the structural skeleton and the molecular network, arranged in parallel. The skeleton, consisting of the crystalline lamellae, interlamellar crystalline bridges and taut-tie molecules, is assumed to be responsible for the majority of the stiffness within the polymer. The molecular network intermingles with this skeleton and its contribution to the modulus is considered insignificant. It is, however, responsible for the retractive stresses.

The thermally induced strain (thermal expansion) in such a model has an extra component dependent on the competition between the sample stiffness and the retractive force, both of which change with temperature. Generally the thermal expansion, α , can be expressed:

$$\alpha = -\frac{\sigma}{E^2} \frac{dE}{dT} + \frac{1}{E} \frac{d\sigma}{dT} + \alpha_0 \quad (1)$$

where σ is the stress, E the tensile modulus and α_0 the intrinsic thermal expansion coefficient of the sample.

Although the temperature dependence of the tensile modulus can be measured experimentally, the temperature dependence of the stress is unknown. For simplicity it is assumed that the polymer network behaves similarly in manner to an ideal rubber, in which case $\sigma = -BT$, where B is the network stress parameter. Using this assumption the thermal expansion can be written:

$$\alpha = B \left[\frac{T}{E^2} \frac{dE}{dT} - \frac{1}{E} \right] + \alpha_0 \quad (2)$$

For convenience the term, $[(T/E^2)(dE/dT) - (1/E)]$ is replaced by the symbol Θ , in which case equation (2) becomes

$$\alpha = B\Theta + \alpha_0 \quad (3)$$

A simple plot of the thermal expansion coefficient, α , against Θ , measured over a range of temperatures, will therefore give a straight line, with gradient, B , related to the 'tightness' of the network. The intercept or intrinsic thermal expansion coefficient, α_0 , depends on the structure of the sample, but should be a constant for a given structure.

Examination of the network model

The applicability of the network model was tested on the low molecular weight material. The modulus (Figure 3) and thermal expansion (Figure 5) results of samples with a common pre-extrusion morphology but extruded to a range of deformation ratios were combined to give the results presented in Figure 6. Values for the network stress parameter, B , and intrinsic thermal expansion coefficient, α_0 , obtained from these plots are given in Table 2. The results suggest that the model works exceptionally well for these samples. First, there is a reasonably good linear relationship for each of the samples. Secondly, the magnitude of α_0 in each of the samples is less than that of the crystal expansion coefficient¹⁶ ($-12 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$), and finally the network stress parameter B increases steadily with increasing deformation ratio. This success is the justification for extending the analysis to examine samples which have all

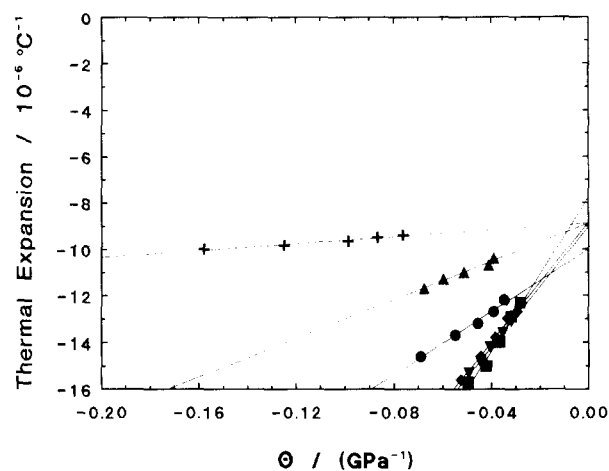


Figure 6 Application of the network model to oriented samples of pressure annealed polyethylene (Grade A). See Figure 3 for key to samples

been extruded to the same level but which have been subjected to different annealing histories. Changes in B will now reflect the effect of annealing on the molecular network.

Effect of annealing

The effect of altering in turn each of the main annealing parameters, namely pressure, temperature and time, was only investigated in the low molecular weight Grade A. Before considering the effects of changing these parameters it is useful to note the thermodynamic consequences. By reducing the pressure or increasing the temperature, material in the orthorhombic phase can be taken into the hexagonal phase, in the process undergoing considerable morphological changes. If annealing is performed on the boundary between the orthorhombic and hexagonal phases a transitional morphology is produced¹⁷. The classic anabarc morphology is produced if annealing is performed deeper in the hexagonal phase.

Typical results, combining thermal expansion and mechanical measurements using the network model, for variations in the annealing pressure only, are shown in Figure 7. Clearly the behaviour is now quite complicated but the model still appears to hold, although there are considerable variations in both the intrinsic thermal expansion (intercept) and the network parameter B (gradient). Values for these parameters are presented in Table 3, from which some general observations can be noted. The value for α_0 changes abruptly from

Table 2 The effect of deformation ratio on the network model parameters

Extrusion ratio (R_n)	Intrinsic thermal expansion (α_0) (10^{-6} K^{-1})	Network stress parameter (B) ($10^{-3} \text{ MPa K}^{-1}$)
5	-8.9	7.3
7	-8.9	42.0
10	-10.0	69.0
14	-9.0	131.0
16	-8.9	131.0
18	-7.9	143.0

Samples of Grade A annealed at 500 MPa and 234°C for 1 h, before being extruded to the ratio shown

$-0.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $-8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for a change in the annealing pressure from 540 MPa to 515 MPa. Reducing the annealing pressure further has little effect on α_0 , its value remaining constant at about $-8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. This rapid change in α_0 corresponds to similarly large changes in crystallinity¹⁷. Pressure annealing also leads to changes in the molecular network parameter, B , as can be seen from the different gradients in *Figure 7*. The calculated values of B (*Table 3*) have a large error of $\pm 20 \text{ MPa }^\circ\text{C}^{-1}$, but nonetheless a clear trend to lower values can be discerned and this continues at lower annealing pressures when α_0 has effectively reached a constant value. This implies that a further breakdown in the molecular network occurs for annealing deeper in the hexagonal phase.

The general conclusions on the effect of annealing within the hexagonal phase are confirmed by the changes observed on altering the annealing temperature, as can be seen in *Figure 8*, where the change in network stress is plotted, and *Table 3*, which includes results for the intrinsic thermal expansion. Bearing in mind that an increase in the annealing temperature takes the polymer into the hexagonal phase, it can be seen that the changes in α_0 and B parallel those changes obtained when pressure is used as the mechanism for entry.

The effect of annealing time on the network stress is shown in *Figure 9*. After an initial rapid change, a gradual decrease in the network stress parameter B accompanies the use of longer annealing times. Changes in the intrinsic thermal expansion are given in *Table 3*. The initial change in the annealing time from 5 to 15 min, produces an increase in the magnitude of α_0 , but for annealing times in excess of 15 min, there is very little change.

Molecular weight effects

The behaviour of the other molecular weight grades has been investigated for changes in the annealing pressure only. Plots similar to *Figure 7* have been produced but only results for the highest molecular weight material (Grade D) are included here (*Figure 10*) because they are quite different from those of Grade A, shown earlier. Although the analysis still produces good linear relations, the results for Grade D are

fundamentally different in that the intrinsic thermal expansion is positive. This is not explicable on the basis of a parallel model and indicates a failure of the analysis. With the exception of some samples annealed well away from the hexagonal phase, the other grades of material generally do not suffer from this criticism. A fuller explanation for the breakdown of the model will be given later.

Rather than considering plots of the type shown in *Figures 7* and *10* it is more useful to consider directly the effects on the intrinsic thermal expansion and the network stress parameter, and this is done in *Table 4* and *Figure 11*. The general trends when varying the annealing pressure, observed earlier in Grade A, are seen in Grades B and C, although the degree of change is less pronounced. Two trends are evident in *Figure 11*. First, the particular annealing pressure at which the changes become significant moves to lower values as the molecular weight is increased. Secondly, there is a general trend for the value of B to increase with molecular weight. This is attributable to increases in the entanglement density accompanying the move to higher molecular weight. The initial drop in entanglement density, shown on moving from Grade A to Grade B, is probably explained by the fact that the higher molecular weight materials are all derived from powder morphologies.

DISCUSSION

The extruded samples of polyethylene examined here generally possess extremely large negative values for the thermal expansion in the extrusion direction. In particular, at deformation ratios greater than 10 the macroscopic thermal expansion coefficient ($-16 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) is considerably more negative than that reported for the c-axis of the polyethylene crystal ($-12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). The most obvious explanation for this involves additional retractive forces within the polymer¹⁸.

Choy *et al.*¹⁹ have suggested that this additional retractive force arises from rubber-like forces produced by taut tie-molecules acting between lamellae separated by inter crystalline bridges. The model assumes a composite structure in which the tie-molecules, inter

Table 3 The effect of annealing on the network model parameters

Annealing pressure (MPa)	Annealing temperature ($^\circ\text{C}$)	Annealing time (min)	Intrinsic thermal expansion (α_0) (10^{-6} K^{-1})	Network stress parameter (B) ($10^{-3} \text{ MPa K}^{-1}$)
480	234	60	-7.7	4.3
500	-	-	-8.9	42.4
515	-	-	-7.0	57.3
540	-	-	-0.9	54.1
500	232	60	-3.6	66.2
-	234	-	-8.9	42.4
-	236	-	-8.3	14.0
-	238	-	-9.2	10.2
500	234	5	-2.4	120.0
-	-	15	-7.0	82.7
-	-	60	-8.9	42.4
-	-	300	-8.3	33.4

All samples are of Grade A annealed under the stated conditions and then extruded to a deformation ratio of 7

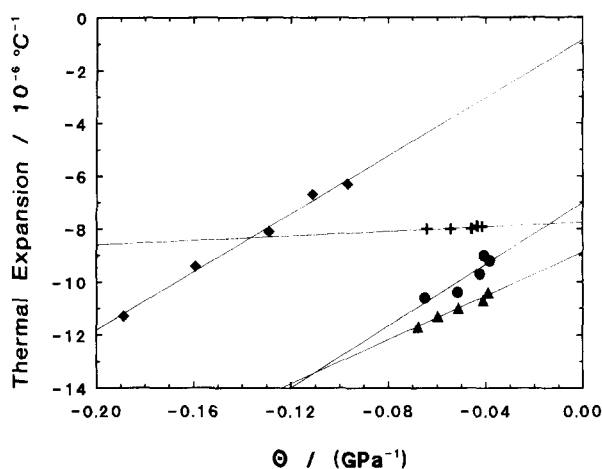


Figure 7 Application of the network model to samples of pressure annealed polyethylene (Grade A), subjected to different annealing histories. All samples extruded to deformation level 7 after annealing for 1 h at 234°C and pressure: +, 480; ▲, 500; ●, 515; ◆, 540 MPa

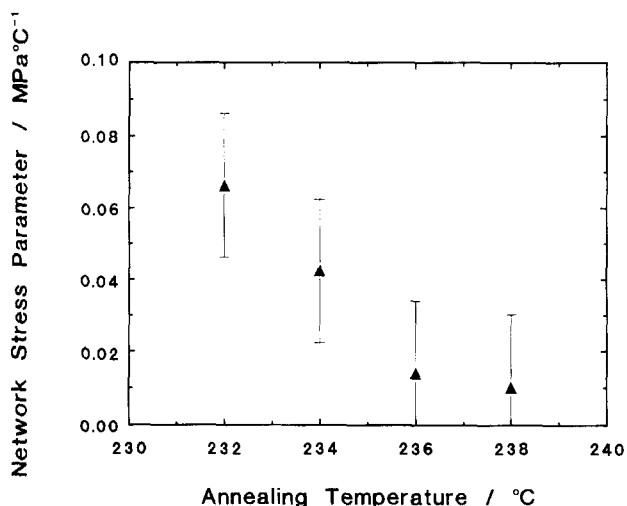


Figure 8 Variation in the network stress parameter for samples of pressure annealed polyethylene (Grade A), as a function of annealing temperature. All samples extruded to deformation level 7 after annealing for 1 h at 500 MPa and the temperature shown

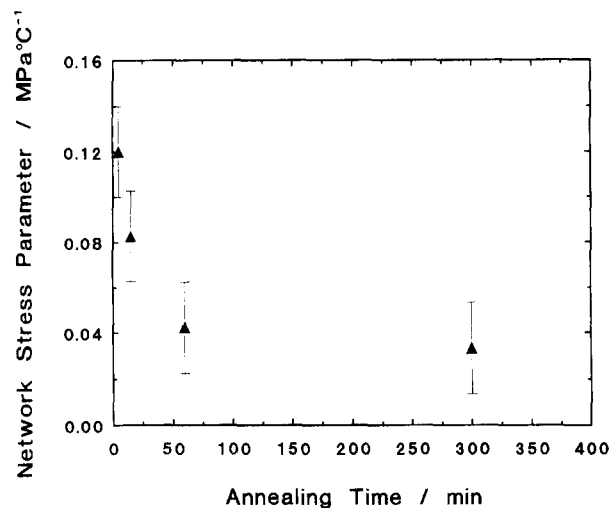


Figure 9 Variation in the network stress parameter for samples of pressure annealed polyethylene (Grade A), as a function of annealing time. All samples extruded to deformation level 7 after annealing at 234°C and 500 MPa for the time shown

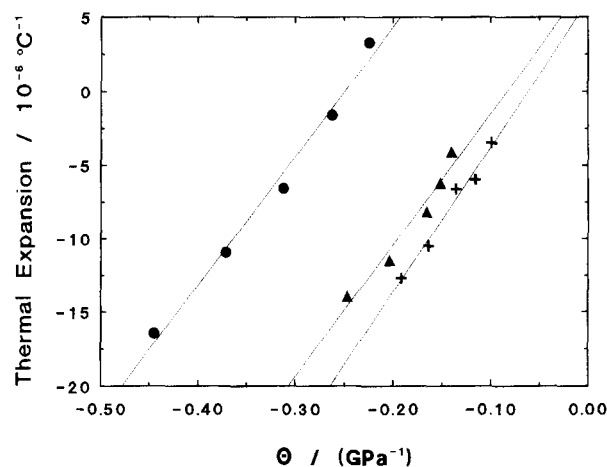


Figure 10 Application of the network model to samples of pressure annealed polyethylene (Grade D), subjected to different annealing histories. All samples extruded to deformation level 7 after annealing for 1 h at 234°C and pressure: +, 450 MPa; ▲, 480 MPa; ●, 500 MPa

crystalline bridges and the amorphous material are all placed mechanically in parallel. The main crystalline lamellae are placed in series with these components. There are however, two significant problems with this model¹⁴. First the internal forces that are required from the tie-molecules, are considerably larger than those that have been observed in shrinkage force experiments. Secondly, the large tie-molecule fraction, required to provide the shrinkage force, would also be required to provide considerably higher than reasonable stiffness to the polymer.

To overcome these problems, Orchard *et al.*¹⁴ have proposed that the stiffness of the polymer is provided by the main structural skeleton and the internal retractive stresses are produced by the molecular network, operating in parallel. This model can explain both the large negative thermal expansion and its variation with temperature, which is attributable to the different temperature dependences of the sample stiffness and the entropically based retractive force. A possible

weakness of the model is the simplification introduced by assuming a linear relation between σ and T , i.e. $\sigma = -BT$, based on ideal rubber elasticity. The parameter, B , characterizing the molecular network, depends only on the crosslink density and the degree of orientation. These two effects are separable and for neo-Hookean behaviour the relation is:

$$B = Nk \left(\lambda^2 - \frac{1}{\lambda} \right)$$

where λ is the draw/extrusion ratio, N the crosslink density and k Boltzmann's constant.

The validity of the model can be tested by considering the effect of orientation separately. The only difference between samples considered in Figure 6 and Table 2 is the level of orientation imposed on the original network. All samples have been subjected to identical annealing histories and therefore have similar pre-extrusion morphologies and network structures. When the data in Table 2 is plotted in the appropriate form, Figure 12,

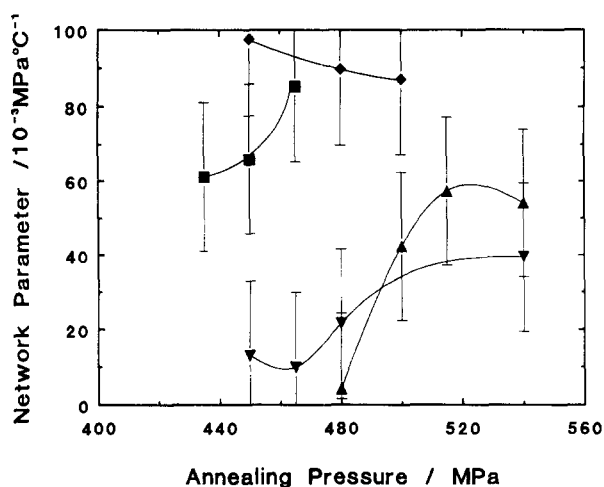


Figure 11 Variation in the network stress parameter for different molecular weight samples of pressure annealed polyethylene as a function of annealing pressure. See *Figure 4* for key to samples

Table 4 Network parameters for different molecular weight grades

Grade	Annealing pressure (MPa)	Intrinsic thermal expansion (α_0) (10^{-6} K^{-1})	Network stress parameter (B) ($10^{-3} \text{ MPa K}^{-1}$)
B	450	-8.8	14.0
	465	-8.1	8.9
	480	-6.5	21.6
	540	-2.3	39.5
C	435	-5.6	61.1
	450	-5.8	65.8
	465	-5.2	85.2
D	450	+5.9	97.6
	480	+7.5	89.7
	500	+22.2	87.1

All samples were annealed for 1 h at 234°C and the pressure shown before being extruded to a deformation ratio of 7

neo-Hookean behaviour is clearly demonstrated, although at the higher draw ratios there does appear to be a slight deviation, possibly due to chain slippage. The agreement justifies the assumptions used and lends

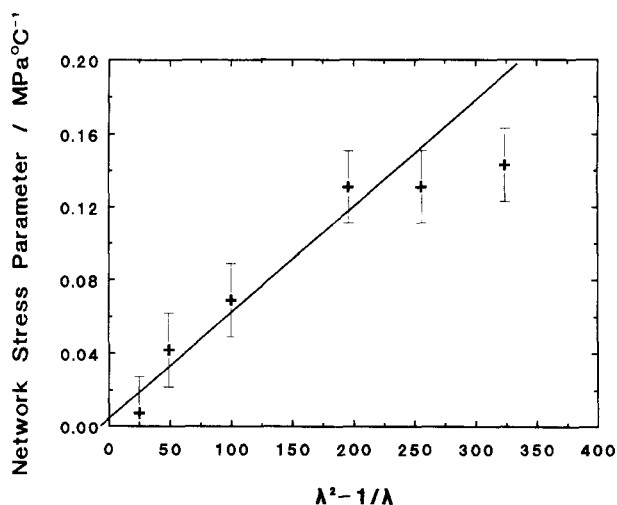


Figure 12 Variation in the network stress parameter with deformation ratio, λ , in pressure annealed polyethylene (Grade A)

confidence to the belief that examination of samples drawn to identical levels of deformation but subjected to different annealing histories, can probe changes in B and hence N resulting from the specific annealing conditions.

Systematic changes in pressure, temperature and time, for conditions in the vicinity of the orthorhombic hexagonal boundary, produce changes in both the basic structure and the network. Morphological analysis¹⁷ of samples of Grade A confirms that the pronounced changes in α_0 , seen when either the annealing pressure is decreased or the temperature increased, occur as the pre-extrusion morphology develops a transitional nature. This morphology is indicative of annealing on the border between the orthorhombic and hexagonal phases and is accompanied by pronounced increases in the crystallinity. This concurrent increase in crystallinity adequately explains the change in α_0 . The high negative thermal expansion of the oriented crystals dominates the positive thermal expansion of the remnants of any non crystalline regions. Deeper annealing within the hexagonal phase does not affect the crystallinity and consequently α_0 also remains relatively unaffected.

These structural changes are accompanied by the development of a less restrictive network, as indicated by the decrease in B , and hence N . However, the molecular network is influenced by annealing within the hexagonal phase and not just on the orthorhombic hexagonal phase boundary as was the case for α_0 . This is not too surprising because, although the crystallinity remains relatively constant in this region, continuing structural readjustment¹⁷ is evident in changes in the shape of the melting curves. The reduction in N can be explained by a decrease in the number of chain-entanglements as the chain-extended lamellae are formed. This process is likely to be kinetically determined as the longer chains need time to disentangle, a view supported by the observed drop in the network stress at long annealing times (*Figure 9*).

Smith *et al.*⁹ have shown that there is an increased probability of obtaining chain-entanglements within higher molecular weight grades, and this is supported by the data in *Figure 11*, where an increase in B is observed for higher molecular weight grades. The higher than expected entanglement density predicted for Grade A is probably due to the fact that samples were not produced from powder but rather from pellets. The higher level of chain entanglements in high molecular weight material is also likely to be responsible for the much smaller changes in crystallinity, as longer times will now be needed to satisfy kinetic requirements.

Although the changes produced by reducing the pressure are not as pronounced in higher molecular weight grades, the general behaviour is very similar to that shown by Grade A. It is noticeable, however, that a lower pressure is required to produce significant changes in higher molecular weight grades but this can be explained by the movement of the orthorhombic hexagonal boundary to lower pressure with increasing molecular weight²⁰. The slightly unusual behaviour of Grade C probably arises from its much greater polydispersity complicating matters.

The relation between α_0 and crystallinity in these different grades is illustrated in *Figure 13*. Most samples lie on a single curve although some, specifically those annealed well away from the hexagonal phase as well as

samples of Grade D (not shown in *Figure 13*), do not follow the same trend. A simple linear extrapolation to fully crystalline material gives a thermal expansion of about $-12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, in agreement with that reported for the crystal¹⁶. The fact that the majority of the samples follow a common trend indicates that they are structurally similar with exceptions to this trend being indicative of structural differences. Indeed, as is shown elsewhere¹⁵, such differences do exist, particularly in the case of Grade D. The majority of samples fit a simplified aggregate model, but samples annealed well away from the intermediate phase, as well as samples of Grade D more closely fit a series model. It is therefore reasonable to expect these samples to follow a series model such as that proposed by Choy *et al.*¹⁹ and not the model applied here.

The desire to produce a molecular network which does not restrict the drawability yet remains capable of providing adequate interconnectivity and crystalline orientation has been noted in both melt- and gel-spun materials⁸⁻¹⁰. It is now clear that the annealing process offers a means of altering and optimizing the molecular network so it is appropriate to consider the implications for the subsequent mechanical properties. Values for the modulus of extrudates of annealed samples of different molecular weight are shown in *Figure 4* in terms of the effect of changing the annealing pressure. The modulus reaches a maximum in all cases except one, Grade D, and although the pressure at which the maximum occurs varies, this is related to the position of the hexagonal phase, which varies with molecular weight²⁰. It is shown elsewhere²¹ that the position at which the maximum occurs does not depend solely on the position of the hexagonal phase but also includes a molecular length consideration.

Figure 14 shows how changes in the pressure annealing conditions, and hence the pre-extrusion morphology and molecular network, affect the level of crystallite orientation produced by extrusion to a standard deformation level. All molecular weight grades show a fall in the crystallite orientation, despite being extruded to the same deformation level, as the samples are annealed closer to the hexagonal phase. There is also a drop in the orientation with decreasing molecular weight. Both these observations are consistent with the decrease in the

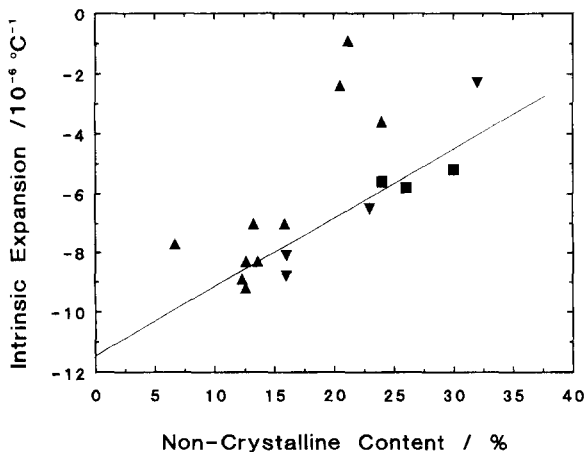


Figure 13 Plot of intrinsic thermal expansion against crystallinity in pressure annealed polyethylene. ▲, Grade A; ▼, Grade B; and ■, Grade C

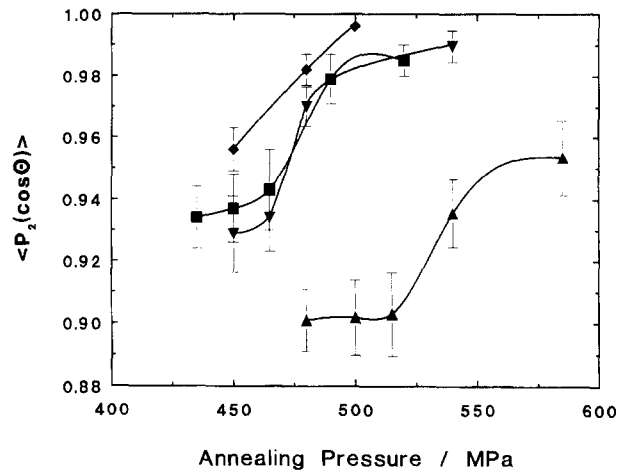


Figure 14 Variation in crystallite orientation, $\langle P_2(\cos \theta) \rangle$, with annealing pressure in different molecular weight polyethylenes. See *Figure 4* for key to samples

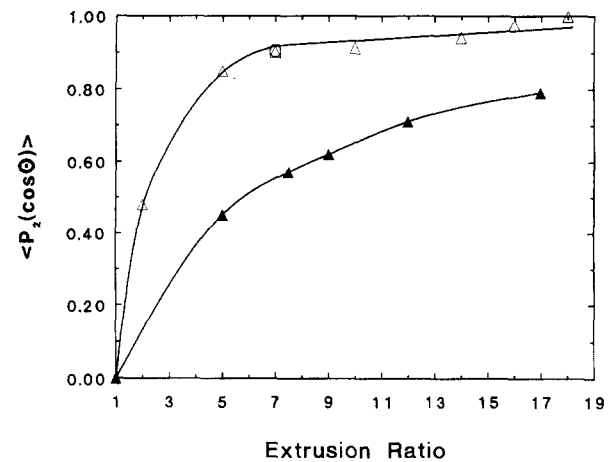


Figure 15 Variation in crystallite orientation, $\langle P_2(\cos \theta) \rangle$, with extrusion ratio. Samples of grade A annealed at 500 MPa and 234°C for 1 h before extrusion. Filled symbols taken from the work of Chuah *et al.*⁵

effectiveness of the molecular network, as manifested in the fall in N . It is possible, however, that structural changes occurring at the same time, i.e. increasing crystallinity and changes in the crystallite aspect ratio, also play a role. Nevertheless, the role of the network in orienting the crystallites is given support by the work of Chuah and Porter⁵, who reported considerably lower crystalline orientation (*Figure 15*) in their annealed samples. That material was of relatively low molecular weight and would be expected to possess a very loose network after annealing within the hexagonal phase.

The low molecular weight samples considered here showed very friable behaviour when annealed within the hexagonal phase, breaking up during the orientation process. This, again, is a reflection of the over destruction of the network which accompanies this type of annealing. The much higher molecular weight materials are not so dramatically affected by annealing within the hexagonal phase, and can consequently withstand much greater depths of annealing. In fact the highest molecular weight material showed an enhanced level of drawability after annealing. Powder compacted samples of this

material could not be extruded to a deformation ratio of 7 unless they were annealed beforehand.

CONCLUSIONS

A simple network model, combining measurements of the temperature dependences of thermal expansion and bending modulus, has been used to examine the effect of annealing in the hexagonal phase on the molecular network. The process of crystal growth accompanying this type of annealing involves an unravelling of the molecular network, with a fall in the crosslink density. Low molecular weight material is most obviously affected by the process. The greater entanglement density of the higher molecular weight material restricts the development of crystallinity and changes in the network crosslink density are considerably less.

Examination of the mechanical properties and crystalline orientation, accompanying these changes in the network, show that it is necessary to satisfy two conflicting requirements. The network must maintain an adequate level of junction points in order to provide effective orientation during deformation, which is essential if good mechanical properties are required. At the same time a network which is overly restrictive inhibits the drawability, a feature observed in high molecular weight material. High pressure annealing, which reduces the junction point density, can be employed to improve the drawability, and has proved successful for ultra high molecular weight material.

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