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The dynamic mechanical relaxation behaviour of polyethylene copolymers cast from solution

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Abstract

Three polyethylene copolymers, which differ widely with respect to their short chain branch content, have been cast from solution and subject to extensive structural and Dynamic Mechanic Thermal Analysis (DMTA) to establish the effect of the morphology on the α-, β- and γ-relaxations.

The results have shown that the α-relaxation temperature, T_α, increases with the lamellar thickness, irrespective of grade, initial solvent concentration or crystallinity and is associated with c-shear within the crystalline lamellae. The β-relaxation temperature, T_β, shows a more complex morphological dependence depending on the grade. The results indicate that this relaxation is associated with interlamellar shear and is determined, to some extent, by fold surface morphology.

The γ-relaxation temperature, T_γ, is shown to be dependent on the initial solution concentration only. It is concluded that this relaxation is associated with short-range motions in the amorphous region, with residual solvent acting to plasticise the amorphous regions.

Keywords: Polyethylene; Dynamic mechanical; Deformation

1. Introduction

The structure-property relations in a wide range of polyethylenes have been extensively studied and a broad range of literature has been published concerning the mechanical relaxation behaviour of these materials. However, there is still a great deal of controversy, which follows the discussion of relaxation mechanisms in polyethylene. Previous results have shown that a wide range of morphological features such as the crystallinity, long period, lamellar thickness, molecular weight and the molecular weight distribution, can affect the relaxation mechanisms within these materials.

It is generally accepted that low and medium density polyethylenes (LDPE, LLDPE and MDPE) exhibit three significant relaxations, referred to as α, β and γ [1]. The α-relaxation occurs at the highest temperature and the γ-relaxation at the lowest. For high density polyethylenes (HDPE) the β-relaxation is usually absent. In addition, under certain conditions the α-relaxation is sometimes seen to consist of two relaxations, referred to as α and α′ [1,2].

The γ-relaxation temperature is typically in the range of −110°C to −150°C and is associated with short-range molecular motions in the amorphous phase [3]. Several molecular models have been proposed to explain the γ-relaxation mechanism. Willbourn [4] has suggested that the γ-relaxation in both amorphous and crystalline polymers is attributed to a restricted motion of the main polymer chain, requiring at least four $-CH_2$ groups on a linear part of the main chain. This has lead to the so-called ‘crankshaft mechanism’ proposed by Schatzki [5] and Boyer [6]. Results obtained for polyethylene and other polymers [7,8] have confirmed the interpretation of the γ-relaxation in terms of the crankshaft mechanism, associated with the amorphous phase.

The β-relaxation temperature typically occurs at, or just below, room temperature. This relaxation is only observed in branched polyethylenes and its magnitude has been shown to decrease as the crystallinity is increased [9]. This relaxation is, therefore, generally attributed to segmental motions in the non-crystalline phase, i.e. either the amorphous or the inter-facial phase.

Popli et al. [10] have suggested that, for polyethylene, the β-relaxation is a consequence of the relaxation of chain units located in the interfacial region. Stackhurski and

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Ward [11–13] and Matthews et al. [14,15] have carried out extensive work on a wide range of polyethylenes and have concluded that the β-relaxation is related to interlamellar shear. Other authors [16,17] have suggested that the β-relaxation is the glass transition in the branched (low density) polyethylenes, although it is generally accepted that in linear polyethylene, the γ-relaxation is the primary glass transition

The assumption that crystal–amorphous interfacial regions are involved in the β-relaxation process implies that the lamellar fold surface morphology must contribute, to some extent, to the β-relaxation process.

The α-relaxation typically occurs at temperatures well above room temperature and approaching the melting temperature of polyethylene. It has been shown that the intensity of the α-relaxation peak increases with crystallinity, and there is general agreement that the α-relaxation is related to the crystalline phase. Several authors [7,10] have suggested that this relaxation is due to the motion of the chains within the crystalline lamellae and it has been clearly shown that the T_α increases as the lamellar thickness increases [10]. The dependence of T_α on both the crystallinity and the lamellar thickness is believed to be due to the fact that for bulk cast polyethylene there is a strong correlation between these two structural parameters as shown by Brooks et al. [18].

Stackhurski and Ward [11–13], Matthews et al. [14,15] and Boyd [3,7,19] have suggested that the α-relaxation in LDPE and MDPE is attributed to c-shear of the macromolecular chains within crystalline lamellae. However, for HDPE, these authors have also shown that the α-relaxation process involves interlamellar shear. These authors suggested that for HDPE the α-relaxation is the same as the β-relaxation observed in LDPE and MDPE, but it has been shifted to higher temperatures due to greater constraints within the inter-lamellar regions. The actual α-relaxation temperature is presumed to increase above the melting temperature, and is therefore not observed. The results of Matthews et al would, therefore, suggest that the interfacial region could influence the α-relaxation as well as the β-relaxation process.

2. Experimental

2.1. Materials and sample preparation

Three grades of ethylene/1-hexene copolymer, characterised by different molecular mass and butyl branch content, were selected for this investigation. The materials were produced by British Petroleum Ltd and supplied in a pelletised form. Details of the materials' characteristics are given in Table 1.

The sample preparation technique used here was based on the procedure developed earlier by Darras et al. [20] to produce polyethylene films cast from solution of decalin. In the present work, various concentrations of polyethylene (varying from 40 to 100 %wt of polymer) were dissolved in decalin at 160°C. The decalin used was a general grade supplied by Aldrich Chemicals.

The solutions were cast to produce flat discs using a steel transfer-moulding device, the gap between the mould plates being 3 mm. The solution was slowly forced into the moulding cavity over a period of approximately 1.0–1.5 min by applying gradually increasing pressure until it reached approximately 15 MPa at the final stage of the process (last 15–20 s). To avoid bubble formation, or, when it was impossible, to locate bubbles near the centre of the cast disc, a 'breathing' moulding technique was used [21,22].

The mould was kept under the pressure for ten additional minutes to allow for some stress relaxation in the melt. Then the mould was cooled to room temperature at a rate of approximately 10°C min^{-1}. The cast polyethylene discs were removed and left in a fume-cupboard for a period of 7–10 days until dry. The polyethylenes were considered dry when their weight stabilised. No noticeable orientation or bubbles were evident from analysis of a dried polyethylene disc under polarised light optical microscopy.

2.2. Crystallinity

Differential Scanning Calorimetry (DSC) was used to determine values for crystallinity and melting temperature. Melting endotherms were obtained using Perkin Elmer Series 7 system at a heating rate of 10°C min^{-1} on samples weighing between 7 and 20 mg. The calorimeter was calibrated using a high-purity indium sample. Five runs were performed for each material to calculate average and standard deviation values.

Crystallinity values were determined using the ratio of the melting enthalpy of the samples to that of a perfect and infinite polyethylene crystal, $\Delta H_m^0 = 290\ \text{Jg}^{-1}$ [23].

2.3. Surface free energy

The surface free energy per unit area of the fold surface, σ_e, was found by using the simplified form of the

Table 1
Chemical characteristics of polyethylene copolymers

Material	M_w	M_n	Branch content	Density, gcm^{-3}
Material A (LLDPE)	126,000	30,300	2.1 mol%	0.920
Material B (MDPE)	206,000	12,900	0.6 mol%	0.938
Material C (HDPE)	138,000	–	–	0.955

Thompson–Gibbs equation [23], such that:

$$\sigma_e = \frac{L_c \Delta H_m^0 \rho_C}{2}\left[1 - \frac{T_m}{T_m^0}\right] \quad (1)$$

where L_c is the Lamellar thickness, T_m the melting temperature, T_m^0 the temperature of melting of an infinite crystal = 140°C [23], ΔH_m^0 the enthalpy of melting per unit mass of an infinite crystal = 290 Jg^{-1} and ρ_C is the crystalline density = 0.997 gcm^{-3} [23].

In a previous paper [24], values of ΔH_m^0, T_m^0 and ρ_C were taken from [25], slightly different from those used by Darras and Seguela [23]. It was decided in this publication to use the latter values to ensure better comparability of our results with those of Darras and Seguela.

The lamellar thickness, L_c, was found using the Small Angle X-ray Scattering (SAXS) method described below. The melting temperature, T_m, was found using the DSC method described above, as with the crystallinity measurements an average of five measurements were taken.

2.4. Lamellar thickness

The long period, D, was measured using the SAXS method. Three cast film samples were tested for each grade corresponding to initial solution concentrations of 40, 70 and 100 wt%. The long period values for the other concentrations were found by linear interpolation of these points.

The experiments were carried out at Station 2.1 of the Daresbury Synchrotron Radiation Source. The beamline was configured with an X-ray wavelength, λ, of 1.52 × and a bandwidth $\Delta\lambda/\lambda \le 4 \times 10^{-3}$. Small angle scattered X-ray photons were detected on an area detector located 3.5 m from the sample. The calibration of the q scale of the detector ($q = 4\pi \sin\theta/\lambda$, where the scattering angle is defined as 2θ) was performed using the first 25 orders of diffraction from wet rat tail collagen. A sixth order polynomial was fitted to the inverse collagen spacings over the detector range. This corrects for the positional nonlinearity of the detector. All diffraction intensities were normalised by the beam flux, which was monitored by an ionization chamber located behind the sample. The two dimensional scattering patterns were found to be symmetric. In order to carry out further analysis, one-dimensional data was obtained through integrating arcs of 20° from the vertical part of the pattern. The experimental data were corrected for background scatter using the scatter from an empty sample holder, and for non-uniform detector sensitivity using the response to a ^{55}Fe X-ray source. Each of the one-dimensional SAXS scattering patterns was Lorentz corrected [26].

The lamellar thickness, L_c, is calculated using the crystalline volume fraction, Φ, and the long period, D, such that:

$$L_c = \Phi D \quad (2)$$

The stem length was then calculated assuming that the chain axis is tilted at an angle 34.5° [27,28] to the fold surface normal.

For Material A, SAXS, DSC and previous Scanning Electron Microscopy (SEM) [29] results have shown that there appear to be two populations of lamellar species, with smaller (infill) lamellae separating the dominant (thicker) lamellae. For Material A, the lamellar thicknesses for the dominant (thicker) lamellae have been found by the method described above. The lamellar thicknesses of the smaller (infill) lamellae have been found from the Thompson–Gibbs equation (Eq. (1)) by taking the melting point from DSC scans and assuming that the surface free energy of the dominant and infill lamellae are the same.

2.5. Dynamic mechanical thermal analysis

The cast polyethylene sheets were cut to give the samples of 4 mm width, and a thickness of between 2.5 and 3 mm. The samples were tested under 3-point bending using a Perkin Elmer Series 7 system, with the distance between the supports being 15 mm, which is the effective length of the samples under load. The storage modulus, loss modulus, and tan δ values were found under a sinusoidally applied strain over a range of temperatures from −140 to +100°C at a heating rate of 5°C min^{-1}. Liquid nitrogen was used to cool the samples and the samples were purged with nitrogen gas throughout the duration of the experiments. The experiments were carried out at four different frequencies: 1, 3.6, 10, and 40 Hz, which approximately correspond to a maximum applied strain-rates of 0.006, 0.023, 0.061 and 0.246 s^{-1} respectively.

3. Results and discussion

The crystallinity, lamellar thickness and surface free energy as a function of the initial solution concentration are shown in Figs. 1–3, respectively, for each of the three grades. The results clearly show that as the concentration of polymer in the initial solution is increased the crystallinity is

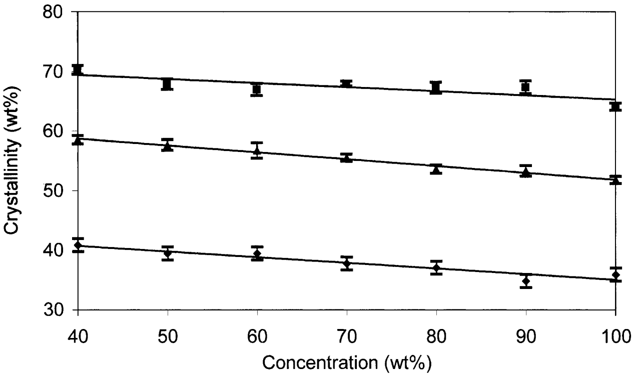

Fig. 1. Crystallinity vs. initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

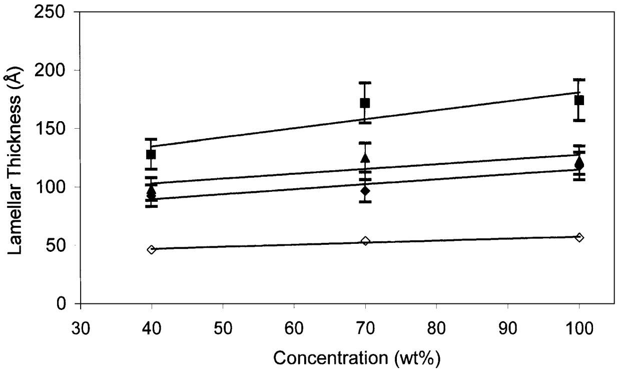

Fig. 2. Lamellar thickness vs. initial solution concentration for Material A, dominant lamellae (◆), Material A, thin lamellae (◇), Material B (▲), Material C (■).

reduced and the lamellar thickness and fold-surface free energy increased. These findings are in agreement with the previous findings of Darras and co-workers [20,23] who have shown for a range of solution cast polyethylenes that there is a nearly linear decrease of fold-surface free energy with increasing dilution.

Darras and co-workers have suggested that the change in the fold-surface free energy is directly related to the fold-surface topology, attributing this change to improvement of regular chain folding. Darras et al. have also found that solution-cast low-density polyethylene showed significant improvement of drawability and reduction of strain hardening with increasing dilution. They attributed this effect to the build-up of regular chain-folded conformations, which result from an easier crystallisation mechanism of long-chain molecules in solution.

Based on the findings of Darras et al., it is reasonable to assume that as the dilution increases the lamellar surface becomes more regular, as dilution creates better conditions for crystallisation in general and formation of more perfect crystals [30].

The storage modulus E', the loss modulus E'' and tan δ measured at a frequency of 3.6 Hz are shown for each of the three materials at three different initial solution concentrations in Figs. 4–6. Similar results are found for the other frequencies employed, however choosing this frequency allows for easier comparison with previously published results.

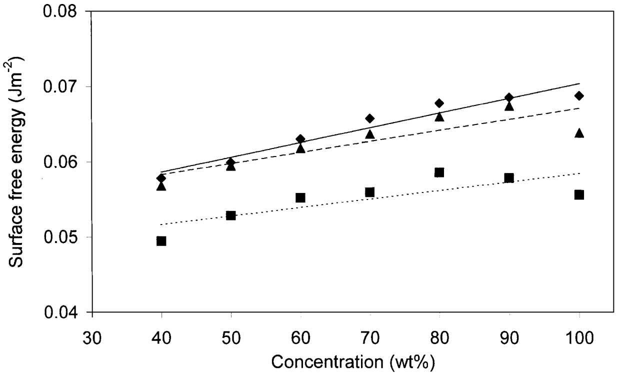

Fig. 3. Lamellar surface free energy vs. initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

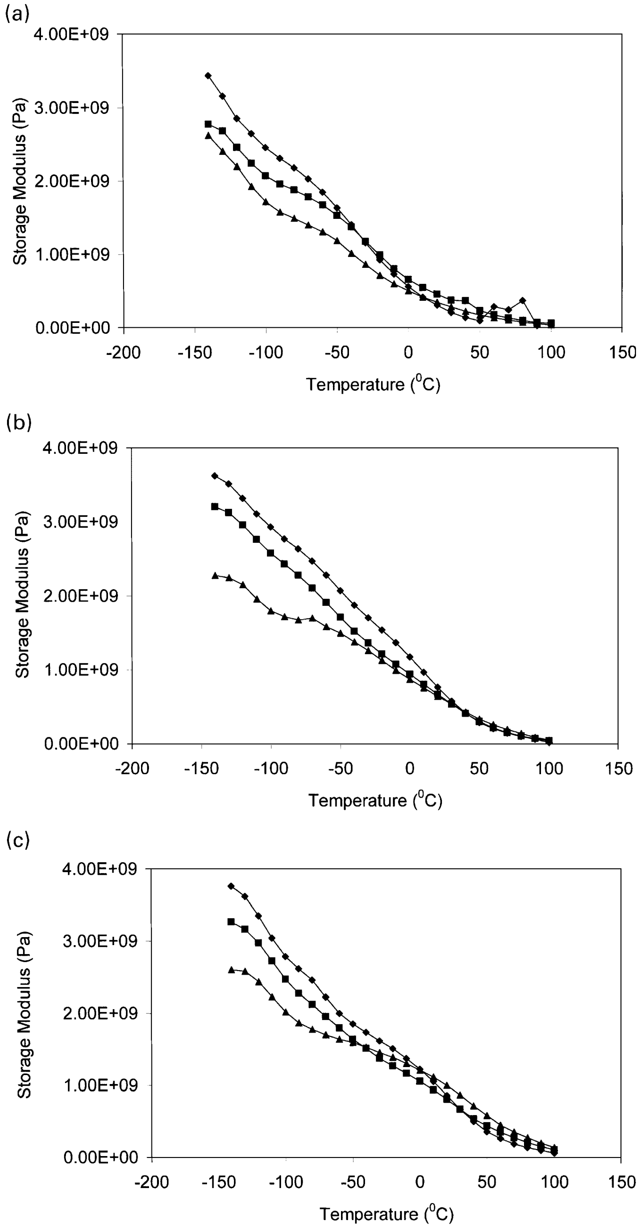

Fig. 4. (a) Storage modulus vs. temperature for Material A cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲); (b) Storage modulus vs. temperature for Material B cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲); (c) Storage modulus vs. temperature for Material C cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲).

The temperatures of the α-, β- and γ-transitions (T_α, T_β and T_γ) were found from the graphs of loss modulus (E'') against temperature, using a method similar to that used by Matthews et al. [31]. Each of the curves was fitted using three Gaussian functions (corresponding to the three relaxations) using a least squares fitting procedure. An example of

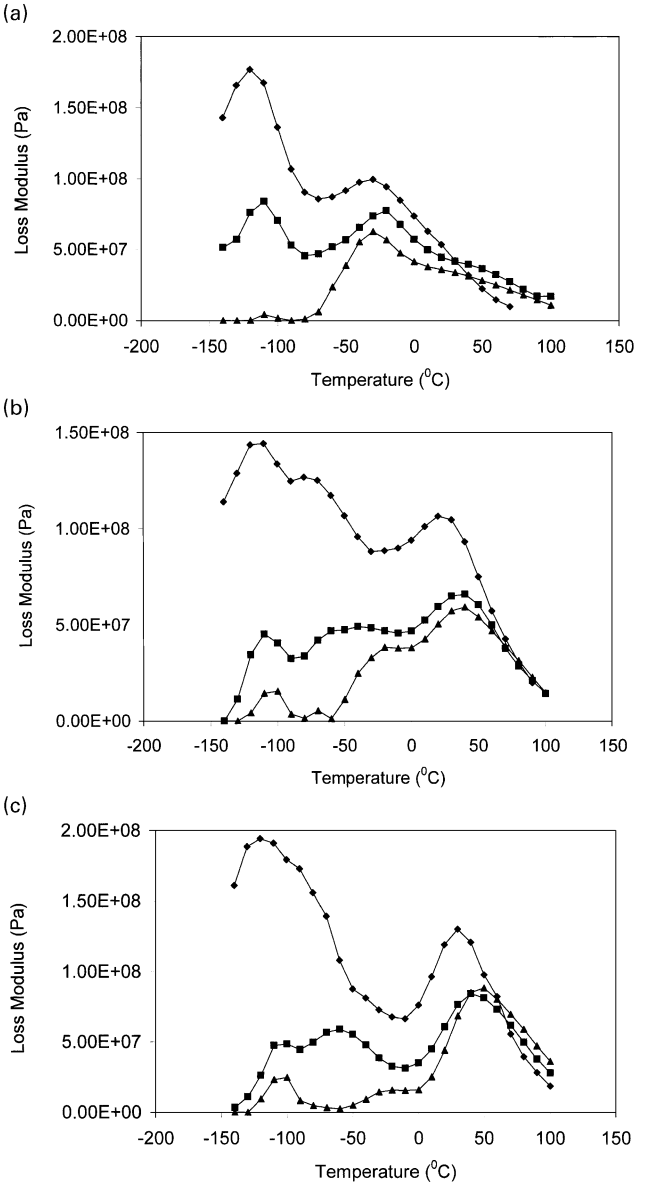

Fig. 5. (a) Loss modulus vs. temperature for Material A cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲); (b) Loss modulus vs. temperature for Material B cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲); (c) Loss modulus vs. temperature for Material C cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲).

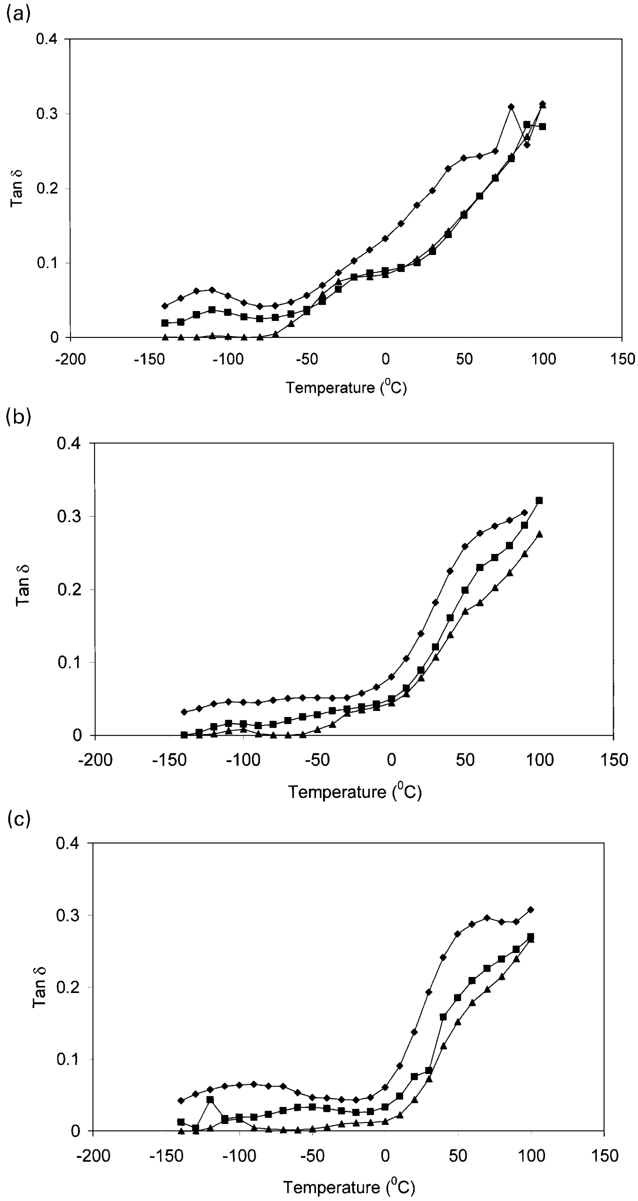

Fig. 6. (a) Tan δ vs. temperature for Material A cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲); (b) Tan δ vs. temperature for Material B cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲); (c) Tan δ vs. temperature for Material C cast from initial solution concentrations of 40 wt% (◆), 70 wt% (■) and 100 wt% (▲).

the fittings is shown in Fig. 7 for Material B cast from an initial solution concentration of 70 wt%.

From the fitting procedure the relaxation temperatures for the three materials at initial concentrations of 40, 70 and 100 wt% were found. Plots of T_α, T_β and T_γ as a function of the initial solution concentration are shown in Figs. 8–10, respectively.

The graphs of the storage modulus (E') against temperature (Fig. 4a,b and c) show that E' is generally higher for the samples characterised by higher crystallinities and lower lamellar thicknesses. However, it should be noted that the dependency of E' on crystallinity is confined to each individual grade of material, and there is no continuity across all of the materials. This result is in agreement with findings of previous authors who have measured the storage modulus for bulk cast polyethylenes under various cooling regimes [14]. These authors concluded that, for individual grades of polyethylene, the storage modulus increases with the crystallinity. It should be noted, however, that for the melt cast polyethylenes previously tested, higher crystallinity also implied higher lamellar thickness. Thus, it is concluded that for small strain deformation the storage modulus of

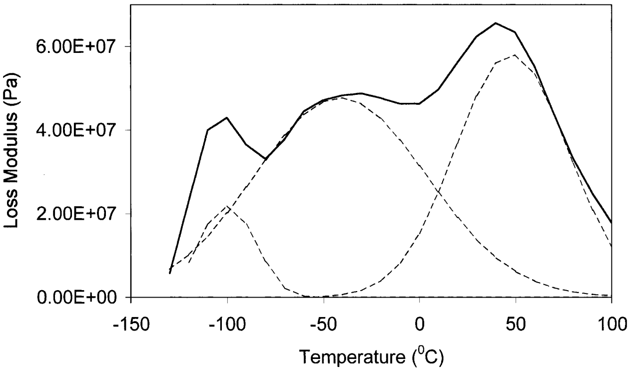

Fig. 7. Loss modulus vs. temperature for Material B cast from an initial solution concentration of 70 wt%. An example of the fittings using Gaussian functions.

the solution cast copolymers is dependent on the crystallinity and not the lamellar thickness. Previous work [24], on these solution cast copolymers, has however concluded that the yield stress is determined by the lamellar thickness and not the crystallinity. This implies a complex relationship between the modulus and the yield stress.

The results in Fig. 10 clearly show that T_γ decreases as the initial solution concentration is decreased. As the γ-relaxation is believed to be associated with short-range molecular motions in the amorphous phase then it would be expected that T_γ should be independent of the molecular weight, short chain branch content and other morphological parameters. However it is not, at first sight, obvious why T_γ should decrease with initial solution concentration. It is concluded that as the initial solution concentration is reduced, and the proportion of decalin is increased, then the amount of residual solvent after 'drying' within the amorphous region also increases. It is the amorphous phase, which would primarily contain residual solvent, as the crystalline and surface regions are characterised by smaller free volume. This increased residual solvent is assumed to plasticise the amorphous regions and thus reduce the glass transition temperature [32]. SEM pictures taken of the samples have indicated the presence of residual solvent within the highly dilute materials.

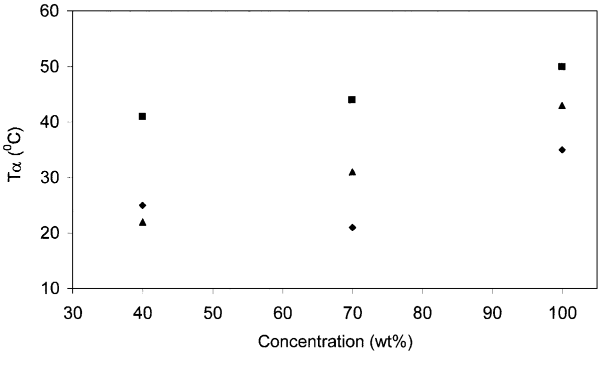

Fig. 8. T_α vs. initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

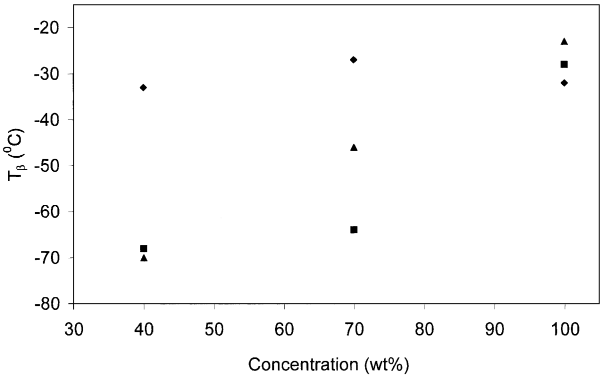

Fig. 9. T_β vs. initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

Following the approach used by Popli et al. [10], T_α is plotted as a function of the lamellar thickness in Fig. 11. Also plotted in this figure is a curve taken from Popli et al. who plotted T_α as a function of the lamellar thickness for a wide range of polyethylenes of lamellar thickness from approximately 80–320Å. It can be seen that there is very good agreement between the results found here and those found by Popli et al. even though by casting from solution we have changed the amorphous and fold surface

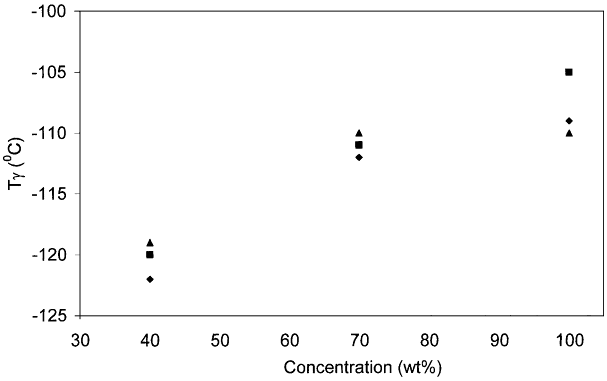

Fig. 10. T_γ vs. initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

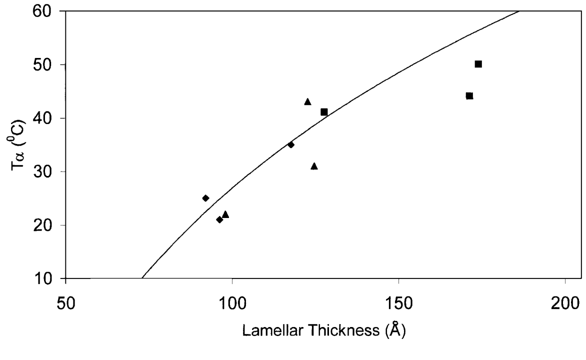

Fig. 11. T_α vs. lamellar thickness for Material A (◆), Material B (▲) and Material C (■), curve shown by solid line taken from [10].

morphologies considerably. Such an agreement is even more remarkable given that Popli et al. used very different materials and techniques.

These results support the proposition that the α-relaxation is associated with c-shear within the lamellar crystals, in agreement with previous authors [10,15], and that T_α is determined by the lamellar thickness only. In addition, the results shown here indicate that the surface morphology does not appear to influence the c-shear process as suggested by Matthews et al. for HDPE.

The results in Fig. 9 show that T_β is relatively constant for the bulk cast polyethylenes (100 wt% polymer) at approximately −20°C, in agreement with the previous findings of Popli et al. [10] who found T_β to be approximately -15 ± 5°C for a wide range of polyethylenes. However as the initial solution concentration is reduced T_β decreases for materials B and C but remains relatively independent of the solution concentration for Material A.

It has been stated above that the β-relaxation process is believed to be associated with the interlamellar shear (l/l shear) of the crystalline lamellae, which should be dependent on the fold surface morphology. Casting these materials from solution is assumed to radically affect the fold surface morphology, which is evidenced by the change in the surface free energy with initial solution concentration. It is therefore unsurprising that T_β changes so significantly with initial solution concentration for Materials B and C. It is thought that as the concentration of the initial solution is reduced the morphology of the fold surfaces becomes more 'perfect' and thus the resistance to inter-lamellar shear and T_β fall as a consequence.

For Material A, it is thought that T_β remains relatively constant due to that fact that this materials has a relatively high short-chain branch content (2.1 mol%) which is excluded from the crystalline lamellae [30]. Therefore, Material A has a significantly large, highly disordered, interfacial region [10] whose morphology is believed not to be significantly affected by casting from solution.

A further complication when considering the morphology of Material A is that for this materials there are believed to be two lamellar populations, with smaller (infill) lamellae separating the dominant (thicker) lamellae [24,29]. The lamellar thickness of the dominant and infill lamellae is within the approximate range 90–120 Å and 40–60 Å respectively. If we again look at the curve of T_α against the lamellar thickness from Popli et al. [10], then it can be seen that the infill lamellae fall within the thickness region where T_α and T_β overlap (approximately −15°C). Therefore the actual peak observed may be a super-position of the α and β-relaxation peaks and as a result the behaviour may be affected. However, no direct evidence of this has been observed.

The fact that T_β is constant for all of the bulk cast (100 wt% concentration) materials is interesting. The surface free energy of the bulk cast materials increases with increased branching content, implying a significant difference between the three copolymer grades. In addition the change of surface free energy with concentration is greatest for Material A, and yet this material shows the smallest change in T_β. These findings would suggest that the surface free energy is not a reliable measure of those morphological features that affect the mechanical behaviour, but moreover, is just an indicator of morphological change.

SEM was carried out on samples cast from 40, 70 and 100 wt%-solutions. The results obtained show that Material A is characterised by banded spherulitic structure, whereas Materials B and C exhibit axialitic structure. The shape and dimensions of these supermolecular structures do not appear to change considerably and therefore are believed not to affect the results obtained and discussed in the present paper. The results of the supermolecular morphology will be presented and discussed in a separate paper later.

4. Conclusions

The DMTA results obtained for three grades of polyethylene copolymer has shown that three relaxation temperatures are observed, in agreement with previous workers. The γ-relaxation is associated with short range motions in the amorphous phase. T_γ is shown to increase as the initial solution concentration is decreased, this is believed to be due to the plasticising effect of residual solvent in the cast materials. The β-relaxation is associated with inter-lamellar shear and is thought to be dependent on the lamellar fold surface morphology. However, quantitative analysis using the surface free energy as a measure of the fold surface morphology proved elusive. The α-relaxation is associated with c-shear within the crystalline lamellae and is dependent only on the lamellar thickness in agreement with previous workers. The lamellar fold surface morphology does not affect the α-relaxation process.

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