

# Effects of crystallinity and stress state on the yield strain of polyethylene

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## Abstract

The yield strain has been measured over a wide range of temperatures for four polyethylene grades which differ with respect to both their short chain branch content and their molecular weight. The results have shown that all the materials exhibit a transition in their mechanical behaviour at sub-ambient temperatures. The transition temperature is shown to increase as the crystallinity is increased. It is proposed that this transition temperature is related to an interlamellar shear process. The yield strain measured over a range of temperatures generally increases as the crystallinity is reduced. © 1999 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Previous work [1–4] carried out on a range of polyethylene materials which differed mainly with respect to their short chain branch content above room temperature and at applied strain rates of less than  $10^{-1} \text{ s}^{-1}$  has shown that all the materials exhibited two yield points. The first marks the onset of temporary plastic deformation and is associated with a recoverable reorientation of the lamellae, and the second with the onset of permanent plastic deformation which is associated with the destruction of the lamellae by a process of c-shear. The mechanical behaviour of the materials can be adequately described using a model of two non-linear Maxwell elements in parallel. The behaviour was found to be dependent on the thermal history of the materials, the testing temperature and strain-rate. In the temperature and strain-rate window investigated the structural and mechanical results are consistent. Drawing of the materials in tension showed that each of the material formed stable necks and exhibited cold drawing behaviour.

The mechanical behaviour is known to change markedly as the temperature is reduced or the strain-rate increased, changing from the initial necking and cold drawing behaviour to ultimate failure in a brittle manner. Recent results by Brooks et al. [5] have shown that for quenched polyethylene samples the yield strain shows a sudden transition in behaviour as the temperature is reduced. This transition

temperature was found to be dependent on both the material and the applied strain-rate. Mechanical analysis of the stress–strain curves both above and below this transition temperature shows a clear change in the mechanical behaviour from the non-linear visco-elastic behaviour above the transition temperature to elastic–plastic behaviour below. Structural analysis of the deformation processes above and below the transition shows that the initial reorientation process seen above the transition temperature was not observed below the transition temperature.

The focus of the present publication is to extend the previous work by considering how the temperature dependence of the yield strain is affected by changes in the crystallinity, by considering both the quenched and the slow-cooled materials. Experiments have also been carried out in compression to establish if the transition temperature is affected by the state of applied stress and strain.

## 2. Experimental

### 2.1. Sample preparation

Four grades of polyethylene with markedly different degree of short chain branching content and molecular weight were selected for investigation. The polymers were supplied by BP Chemicals Ltd. The four grades of polyethylene are identical to those used in the previous publications [1–5]. Full details of the materials are shown in Table 1.

Following established procedures in our laboratory, samples suitable for tensile testing were prepared by

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Table 1  
Chemical characteristics of polyethylene grades

Material	$M_w$	$M_n$	Branch content/1000°C	Crystallinity (%)	Density ( $\text{kg m}^{-3}$ )
Material A	126 000	30 300	21	36.7(Q), 39.8(SC)	920
Material B	206 000	12 900	6.2	53.1(Q), 56.1(SC)	938
Material C	131 000	19 100	<0.1	72.9(Q), 76.3(SC)	962
Material D	395 000	32 800	<0.1	59.6(Q), 62.1(SC)	955

compression moulding 0.5 mm thick sheets at 160°C, then either quenched in cold water or slow cooled, at approximately 2°C/min, to room temperature. The materials for compressive analysis were moulded sheets, compressed using a semi-positive technique to give sheets of approximately 12 mm thickness and then slow-cooled at approximately 2°C/min to room temperature.

## 2.2. Mechanical analysis

### 2.2.1. Tensile deformation

Dumbbell samples with an effective length of 20 mm and a width of 4.8 mm, were cut from the compression moulded sheets (quenched and slow-cooled). These were then subjected to tensile deformation at an initial strain-rate of either  $2.08 \times 10^{-3} \text{ s}^{-1}$  on an Instron testing machine or at  $8.3 \text{ s}^{-1}$  on a servo hydraulic machine to simulate “impact” conditions. The low temperature tests between 0 and  $-120^\circ\text{C}$  were conducted in a nitrogen environment.

The yield stress and strain values were usually calculated from the maximum on the force-elongation curves obtained. If no maximum was observed, then the yield point is calculated using the combined Brereton–Considère approach described in a previous publication [1]. The yield point predicted by the Brereton–Considère approach in each case corresponds to the first yield point.

### 2.2.2. Compression deformation

The samples for compression testing were machined into cylinders 12 mm in length and 6 mm in diameter from the 12 mm thick sheet, to give an aspect ratio of 2:1. These

samples were subjected to compressive deformation on an Instron mechanical testing machine. Yield stress values were only obtained in compression for Material C at a strain-rate of  $3.5 \times 10^{-3} \text{ s}^{-1}$  over a range of temperatures.

Under compressive deformation the yield stress and strain values were always calculated using the Brereton–Considère approach as no maximum was seen at the yield point in compression.

### 2.3. Dynamic mechanical thermal analysis, DMTA

The DMTA work was carried out using a Rheometrics RSA II solids analyser. This uses a linear servo motor to provide an oscillatory deformation to the sample at a precise strain and a matching transducer which detects the material’s response as a force. The samples were machined from the slow-cooled slabs to a thickness of 5 mm and a width of 10 mm. These were analysed in three point bending with the separation of the loading points set at 48 mm, which is the effective length of the sample during testing. The samples were pre-stressed so that they would remain under stress over the entire range of movement of the head using the procedures recommended by Rheometrics.

The samples were tested over a range of temperatures from  $-160^\circ\text{C}$  to the melting point, with measurements being made at 10°C intervals. A 15 min “soak time” was allowed at each temperature, before testing at three angular frequencies: 1, 10 and 100  $\text{rad s}^{-1}$ , corresponding to maximum applied strain-rates of,  $10^{-3}$ ,  $10^{-2}$  and  $10^{-1} \text{ s}^{-1}$  on the outer surfaces of the beam. The results obtained allow the moduli and  $\tan \delta$  values to be found for the materials over the range of temperatures employed.

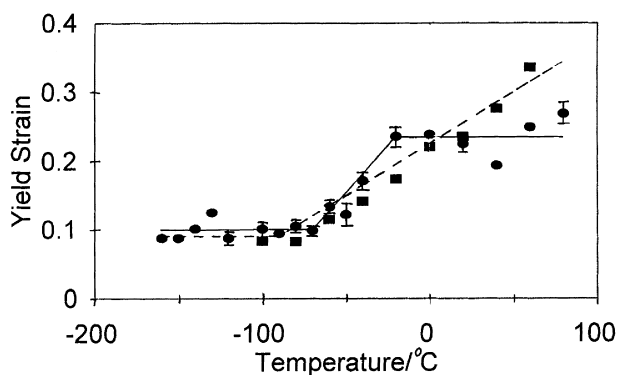


Fig. 1. Yield strain against temperature for Material A. Strain-rate =  $2.08 \times 10^{-3} \text{ s}^{-1}$ : ●— quenched; ■— slow-cooled.

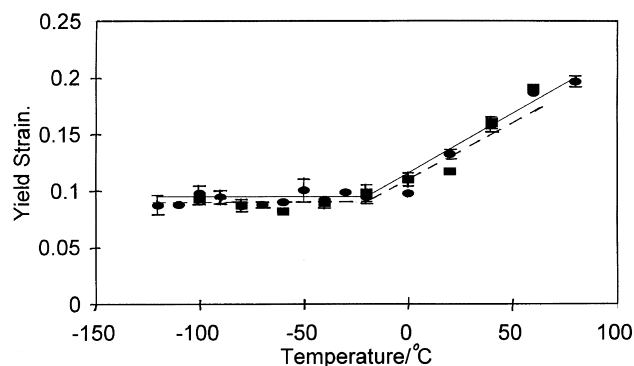


Fig. 2. Yield strain against temperature for Material B. Strain-rate =  $2.08 \times 10^{-3} \text{ s}^{-1}$ : ●— quenched; ■— slow-cooled.

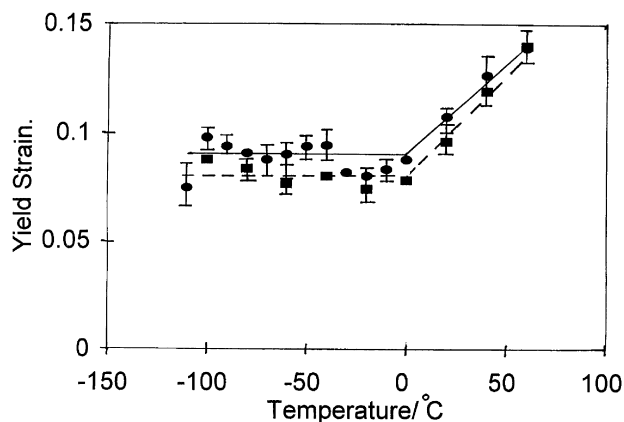


Fig. 3. Yield strain against temperature for Material C. Strain-rate =  $2.08 \times 10^{-3} \text{ s}^{-1}$ : ●— quenched; —■— slow-cooled.

### 3. Results and discussion

The yield strain for each of the grades of polyethylene was found as a function of the testing temperature for the quenched and slow cooled materials at two very different strain-rates: 8.3 and  $2.03 \times 10^{-3} \text{ s}^{-1}$ . The yield strain as a function of temperature for both the quenched and slow cooled materials under an applied strain-rate of  $2.03 \times 10^{-3} \text{ s}^{-1}$  is shown in Figs. 1–4. The results at the higher strain-rate were similar to those found at the lower strain-rate and are omitted for succinctness. The yield strain measurements for Material C (SC) in both tension and compression are shown in Fig. 5, the tensile yield strain is measured at an applied strain-rate of  $2.03 \times 10^{-3} \text{ s}^{-1}$  and the compressive yield strain at  $3.5 \times 10^{-3} \text{ s}^{-1}$ .

Previous results [5] have shown that the temperature dependence of the yield strain of the quenched materials in tension is complex. At low temperatures the yield strain is approximately independent of the testing temperature. As the temperature is increased there is a transition temperature, above which the yield strain increases significantly with increasing temperature. The results presented here show that similar results are also found for the slow-cooled materials under similar deformation conditions.

The results show that the yield strain for the quenched

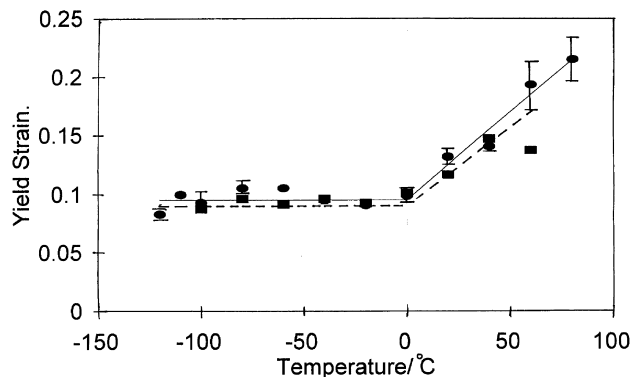


Fig. 4. Yield strain against temperature for Material D. Strain-rate =  $2.08 \times 10^{-3} \text{ s}^{-1}$ : ●— quenched; —■— slow-cooled.

materials is slightly higher than for slow-cooled materials under the same temperature and strain-rate conditions. This can be explained in terms of the differing crystallinities of the quenched and slow-cooled materials. The lower crystallinity of the quenched materials implies that the stiff lamellar blocks are separated by relatively more of the amorphous matrix, through which the stress is transmitted, leading to a higher yield strain for the lower crystallinity (quenched) materials. The transition temperature for each of the materials is shown in Table 2, (values quoted to  $\pm 20^\circ\text{C}$ ). The results show that the transition temperature is dependent on both the grade of the material and the applied strain-rate. The results also show that for the individual grades of polyethylene, the transition temperature is independent of the thermal treatment. However, the transition temperature is seen to increase as the crystallinity is increased for the whole range of materials.

The compressive yield strain values found for Material C show similar behaviour to the tensile yield strain results. However, the yield strain values found in compression are higher than those in tension over the entire range of temperatures. It is believed that this difference may be due, at least in part, to the differing methods used to calculate the yield points in tension and compression. Previous work [2] comparing the tensile yield strain measured from the maximum on the force-elongation curve and the

Table 2  
Transition temperatures identified from yield strain against temperature plots

Material	Thermal treatment	Transition temperature ( $^\circ\text{C}$ )	
		Strain-rate = $2.03 \times 10^{-3} \text{ s}^{-1}$	Strain-rate = $8.3 \text{ s}^{-1}$
Material A	Quenched	-60	-60
	Slow-cooled	-60	—
Material B	Quenched	-20	+20
	Slow-cooled	-20	+20
Material C	Quenched	0	+20
	Slow-cooled	0	+20
Material D	Quenched	0	+20
	Slow-cooled	0	—

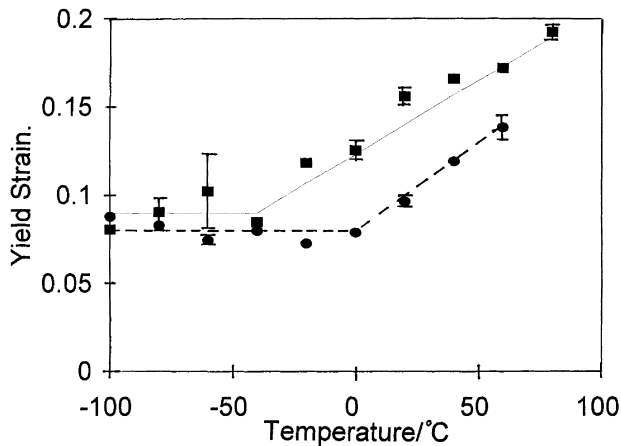


Fig. 5. Yield strain against temperature for Material C (slow-cooled). --●-- in tension, strain-rate =  $2.08 \times 10^{-3} \text{ s}^{-1}$ . --■-- in compression, strain-rate =  $3.5 \times 10^{-3} \text{ s}^{-1}$ .

Brereton–Considère method has shown that there is generally a difference between the two values.

The most important difference between the temperature dependence of the yield strain in tension and compression is that the transition temperature is lower in compression ( $-40^\circ\text{C}$ ) than in tension ( $0^\circ\text{C}$ ). Although the tensile and compressive tests were carried out at slightly different strain-rates, it is not believed that the difference is large enough on its own to give rise to this result.

There is insufficient data available to give an explanation for the relatively large difference between the transition temperature in tension and compression. Previous workers [6,7] have shown that the glass transition temperature,  $T_g$ , for polyethylene increases as the hydrostatic pressure,  $P$ , is increased, such that  $\Delta T_g/\Delta P \approx 0.2\text{--}0.3 \text{ K/MPa}$ . However if these values are used, the difference in the hydrostatic pressure ( $\sigma_y/3$ ) alone between tension and compression for Material C is not only insufficient in magnitude to lead to such a large change in the transition temperature but, more importantly, would lead to the transition temperature being higher in compression than in tension. Although tensile and compressive yield are both manifestations of shear, there may be additional mechanisms operating in tension due to the hydrostatic component of stress.

Recent studies by Matthews et al. [8] have confirmed and elaborated those carried out previously by Stachurski and Ward [9] on oriented samples of LDPE and HDPE. It has been confirmed that the  $\beta$ -relaxation in annealed LDPE sheets shows similar anisotropy to the  $\alpha$ -relaxation process in HDPE, consistent with the interlamellar shear process, i.e. shearing of the lamellae past one another. However, Matthews et al also showed that the activation energies for these processes were very different. The  $\beta$ -relaxation in LDPE showed a very high activation energy, similar to a glass transition process. The  $\alpha$ -relaxation process in HDPE, on the contrary, showed a much lower activation energy, consistent with the c-shear process and similar to

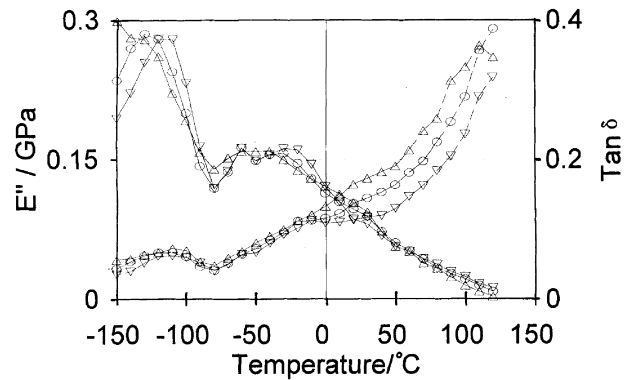


Fig. 6. Loss modulus,  $E''$ , and  $\tan \delta$  as a function of temperature for Material A (slow-cooled) from DMTA. --△-- Modulus  $1 \text{ rad s}^{-1}$ ; --○-- Modulus  $10 \text{ rad s}^{-1}$ ; --▽-- Modulus  $100 \text{ rad s}^{-1}$ ; --△--  $\tan \delta$   $1 \text{ rad s}^{-1}$ ; --○--  $\tan \delta$   $10 \text{ rad s}^{-1}$ ; --▽--  $\tan \delta$   $100 \text{ rad s}^{-1}$ .

that of the  $\alpha$ -relaxation process in LDPE which shows the expected anisotropy for a c-shear process. It was concluded that in HDPE interlamellar shear is always accompanied by c-shear in the lamellae. This conclusion was also reached by Galeski et al. [10] based on detailed X-ray analyses of polyethylene deformation under plane strain compression tests at  $80^\circ\text{C}$ .

The loss modulus and  $\tan \delta$  values at three different strain-rates are shown for each of the four grades of polyethylene in Figs. 6–9.

The maximum applied strain-rate under three point bending, DMTA, is found for the three angular frequencies 1, 10 and  $100 \text{ rad s}^{-1}$  to be approximately:  $10^{-3}$ ,  $10^{-2}$  and  $10^{-1} \text{ s}^{-1}$  respectively, based on an applied strain amplitude on the surface of the samples of  $10^{-2}$ . The temperature at which the interlamellar shear is activated at applied strain-rates of  $10^{-1}$  and  $10^{-3} \text{ s}^{-1}$  has been estimated from the DMTA results. For the high density materials (C and D), where no  $\beta$ -relaxation is observed, it is taken as the lowest temperature at which the  $\alpha$ -relaxation is observed. For the low and medium density materials (A and B), where a  $\beta$ -relaxation is observed, it is taken as the lowest temperature at which the  $\beta$ -relaxation is observed. These values are shown in Table 3 compared with the transition temperatures identified from the plots of yield strain against temperature.

The results in Table 3 show that temperature at which the interlamellar shear is activated (found using DMTA) and the

Table 3

Transition temperatures identified from yield strain compared to temperature at which the interlamellar shear process is activated from DMTA

Material	DMTA		Yield strain	
	$10^{-1} \text{ s}^{-1}$	$10^{-3} \text{ s}^{-1}$	$8.3 \text{ s}^{-1}$	$2.03 \times 10^{-3} \text{ s}^{-1}$
Material A	-60	-60	-60	-60
Material B	+10	-20	+20	-20
Material C	+20	-20	+20	0
Material D	+20	-20	+20	0

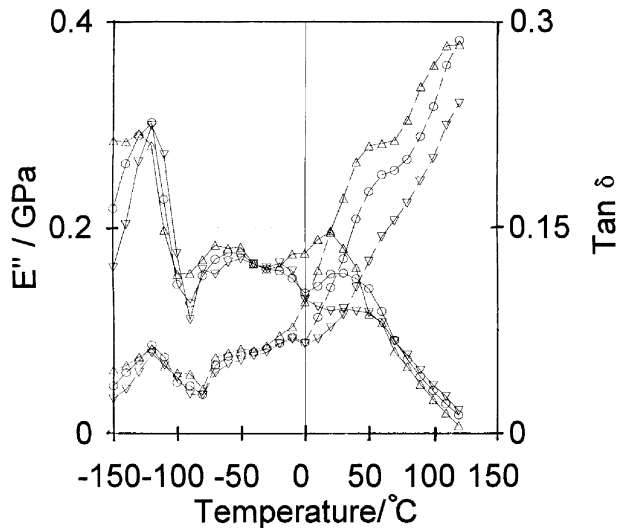


Fig. 7. Loss modulus,  $E''$  and  $\text{Tan } \delta$  as a function of temperature for Material B (slow-cooled) from DMTA.  $\triangle$ — Modulus  $1 \text{ rad s}^{-1}$ ;  $\circ$ — Modulus  $10 \text{ rad s}^{-1}$ ;  $\nabla$ — Modulus  $100 \text{ rad s}^{-1}$ ;  $\triangle$ — $\delta$   $1 \text{ rad s}^{-1}$ ;  $\circ$ — $\delta$   $10 \text{ rad s}^{-1}$ ;  $\nabla$ — $\delta$   $100 \text{ rad s}^{-1}$ .

transition temperature identified from the yield strain results are in good agreement within the error of the experiments (at both strain-rates considered). These results imply that the transition identified from the temperature dependence of the yield strain may be associated with the activation of the interlamellar shear process. It is concluded that the increase in the measured yield strain above the transition temperature is, therefore, due to the greater mobility of the intercrystalline regions which transmit the strain between the lamellae.

It should be noted that although the low frequency DMTA and yield strain measurements were carried out at

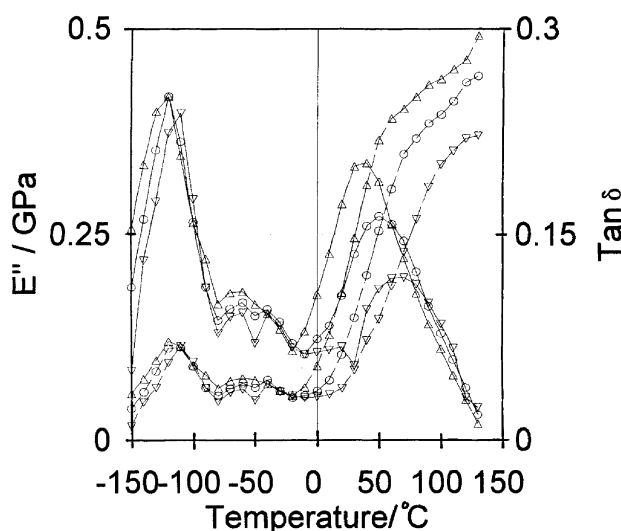


Fig. 8. Loss modulus,  $E''$  and  $\text{Tan } \delta$  as a function of temperature for Material C (slow-cooled) from DMTA.  $\triangle$ — Modulus  $1 \text{ rad s}^{-1}$ ;  $\circ$ — Modulus  $10 \text{ rad s}^{-1}$ ;  $\nabla$ — Modulus  $100 \text{ rad s}^{-1}$ ;  $\triangle$ — $\delta$   $1 \text{ rad s}^{-1}$ ;  $\circ$ — $\delta$   $10 \text{ rad s}^{-1}$ ;  $\nabla$ — $\delta$   $100 \text{ rad s}^{-1}$ .

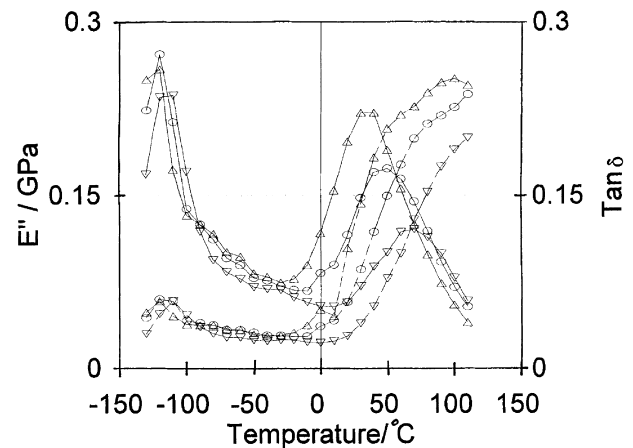


Fig. 9. Loss modulus,  $E''$  and  $\text{Tan } \delta$  as a function of temperature for Material D (slow-cooled) from DMTA.  $\triangle$ — Modulus  $1 \text{ rad s}^{-1}$ ;  $\circ$ — Modulus  $10 \text{ rad s}^{-1}$ ;  $\nabla$ — Modulus  $100 \text{ rad s}^{-1}$ ;  $\triangle$ — $\delta$   $1 \text{ rad s}^{-1}$ ;  $\circ$ — $\delta$   $10 \text{ rad s}^{-1}$ ;  $\nabla$ — $\delta$   $100 \text{ rad s}^{-1}$ .

approximately the same applied strain-rate, the high strain-rate measurements were carried out at very different applied strain-rates of  $8.3 \text{ s}^{-1}$  (yield strain) and  $10^{-1} \text{ s}^{-1}$  (DMTA). Despite this the temperatures identified from the high strain-rate results are still in good agreement.

The yield strain results in Table 3 show that for Materials B, C and D (medium and high density polyethylene) the transition temperature increases between 20 and 40°C as the strain-rate is increased. This is contrast to Material A (low density polyethylene) which shows that the transition temperature for this material is effectively strain-rate independent. This is consistent with the conclusions of Matthews et al. [8] who have shown that the interlamellar shear process has a much higher activation energy than that measured for HDPE.

We have demonstrated in a recent article [11] that the yield stress is a smooth and continuous function of the temperature. No transition is apparent from the plots of the yield stress as a function of temperature, although the transition is apparent from the relationship between the yield stress and modulus. We have proposed two main mechanisms for deformation, namely inter- and intra-lamellar shear, although at this stage we are unable to make a mechanistic link between these and the yield behaviour.

#### 4. Conclusions

Analysis of the temperature dependence of the tensile yield strain for a range of quenched and slow-cooled polyethylenes has shown that a transition is observed at sub-ambient temperatures. Previous work has established that this transition is associated with a change in the mechanical behaviour of these materials, such that above this transition temperature all the materials exhibit non-linear visco-elastic

behaviour and below the transition temperature the materials deform in an elastic-plastic manner.

The results show that the tensile yield strain, at any given temperature, is generally higher for the quenched materials than for the slow-cooled materials. It is therefore concluded that the tensile yield strain increases as the crystallinity of the materials is reduced.

The results also show that the transition temperature increases as the crystallinity is increased for the entire range of samples. However, for each particular grade there were no identifiable differences between the transition temperature of the quenched and slow-cooled samples. It is thought that the differences in crystallinity for each of the materials are not sufficiently large to affect the transition temperature.

Comparison of the transition temperature measured for one of the materials in both tension and compression has shown that the transition temperature is dependent on the state of the applied stress. It is believed that this difference is more likely to be due to geometric factors rather than changes in the hydrostatic pressure.

Analysis of the viscoelastic relaxation processes using dynamic mechanical thermal analysis has concluded that the observed transition is associated with the interlamellar shear process. It is, therefore, concluded that the increase in

the measured yield strain above the transition temperature is due to the greater mobility of the intercrystalline regions which transmit the strain between the lamellae.

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