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A SANS study of the plastic deformation mechanism in polyethylene

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Small angle neutron scattering was used to investigate the role of partial melting and recrystallization in the solid state deformation of polyethylene. Blends containing 4 vol% deuteropolyethylene in protonated polyethylene were deformed in a pure shear mode. The scattering cross section of the undeformed blends was well in excess of that expected for randomly (statistically) dispersed molecules, due to isotopic segregation effects between the deuterated and the protonated species. A significant reduction in the excess scattering was observed as the blends were deformed beyond the yield point. Upon further deformation, the cross section underwent a further modest decrease. Such a reduction is known to occur on melting. The neutron scattering results, hence, support the notion of local melting during the yielding and the subsequent deformation processes.

(Keywords: SANS; plastic deformation; polyethylene)

INTRODUCTION

Two distinctly different mechanisms have been proposed for the plastic deformation in semicrystalline polymers. Flory and Yoon[1] have proposed a partial melting–recrystallization mechanism. Their argument was based on the fact that the chains in neighbouring crystallites are profusely intertangled and these entanglements preclude the relative movement of the crystallites without a local or partial melting. Partial melting, as a consequence of the applied stress, is expected to commence in less perfect parts of the crystallites. It then propagates to the adjacent part as plastic deformation proceeds. It is therefore reasonable to associate the onset of melting with the yield process. Recrystallization immediately follows the partial melting and the reformed crystallites have their chains aligned along the draw direction. In addition, it is well documented[2,3] that the long periodicity of the reformed crystallites reflects the sample temperature during deformation. This observation also provides strong support for the melting and recrystallization mechanism.

The other model proposes that the yield process involves a homogeneous nucleation of screw dislocations within the crystallites. The slip direction, or Burgers vector, of these dislocations is parallel to the chain axis[4,5]. Deformation proceeds by the motion of the dislocations zigzagging between different slip planes to avoid obstacles on the crystallite surfaces.

The present work is an extension of our previous studies[6,7], which used the small angle neutron scattering (SANS) cross section from blends of deuterated polyethylene (PED) and normal (protonated) polyethylene (PEH) to probe the nature of the deformation process in semicrystalline polymers. The scattering theory for such isotopically mixed blends is usually based on the assumption that the centres of gravity of the deuterium-labelled molecules are randomly or statistically dispersed in the unlabelled molecules. Thus, the scattering may be analysed via Zimm or Guinier analysis to give the radius of gyration (R_g) or molecular weight (M_w) via the slope or extrapolated (zero-angle) intercept, $I(0)$. It is well known, however, that departures from a random distribution lead to excess scattering, which results from correlated aggregates (clusters) of labelled and unlabelled molecules. Thus conventional SANS analysis is not strictly valid for such systems and if it is applied to the measured values of slope and intercept, it can give rise to anomalously high values of R_g and M_w, well above the single-chain (molecule) parameters. However, such data may be used to throw light on the deformation mechanisms and our previous work demonstrated that plastic deformation of a partially segregated PED/PEH blend resulted in a significant reduction of the apparent SANS M_w or R_g. It has also been observed[6] that such a reduction in SANS M_w and R_g took place during a melting–quenching process. Hence, the melting–recrystallization mechanism is consistent with the findings of our previous work.

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However, a deformation ratio of 13 was chosen for our earlier work. Consequently, the result could not shed any light on that portion of the deformation process where partial melting begins. In particular the question regarding the yield mechanism, which usually occurs within a strain of 0.1–0.2, was not addressed. In the present work, SANS measurements were conducted on samples deformed just beyond the yield point as well as some with additional deformation. It is the objective of this work to pinpoint the strain where the decrease of SANS molecular weight commences, i.e. where the partial melting–recrystallization mechanism begins.

EXPERIMENTAL

Sample preparation

Samples containing 4 vol% PED ($M_w = 149000$, $M_n = 71000$) in a PEH matrix ($M_w = 150000$, $M_n = 20000$) were solution blended in dichlorobenzene, precipitated in methanol, filtered, dried and melt pressed at 160°C in a vacuum mould. The samples were held at 160°C for 30 min followed by slow cooling, at the rate of ~3°C min^{-1}, to room temperature. A slow cooling process was known to enhance the extent of segregation in the PED/PEH blends. This process resulted in a sample density of 0.954.

Samples were deformed in a set of matched dies at room temperature as described in our earlier work[6,7]. The mode of deformation was a pure shear. Samples were elongated along the x-axis and compressed along the z-axis whereas the dimension along the y-axis remained the same. The ratio λ_z, of sample thickness before and after the deformation was taken as the strain. The thickness of the deformed sample was measured a day after the load was removed to allow for the recovery of the elastic or viscoelastic strain. Hence, the strain reported with the SANS results is the plastic strain. A strain rate of 0.01 s^{-1} was used for all the samples. The stress was calculated as the compression load divided by the instant cross-sectional area of the samples. This deformation process was chosen over the more traditional tensile one for the following reasons. The samples deformed in the pure shear mode are void-free, hence the SANS intensities will not be contaminated by the void scattering. In addition, no deformation takes place along one of the principal strain axes, the y-axis; it was along this axis that the SANS intensities of the deformed samples were taken and a direct comparison can be made between that of the undeformed one. The significance of this point will be elaborated later.

SANS measurements

SANS data were obtained over the range of scattering vectors $0.0033 < q < 0.03$ Å^{-1} on the 30 m instrument at the W.C. Koehler small angle scattering facility of Oak Ridge National Laboratory. The neutron wavelength λ was 4.75 Å ($\Delta\lambda/\lambda = 0.06$) and the sample to detector distance was 19.0 m, with pinhole collimation at the source (1.7 cm diameter) and sample (1.0 cm diameter). For the undeformed sample, the two-dimensional scattering patterns were circularly averaged to yield the one-dimensional form of intensity *versus* q, which is defined as $4\pi/\lambda \sin(\theta/2)$. Here θ is the scattering angle. For the deformed samples, intensity slices of the pattern were taken along the axis of zero strain or the y-axis. After corrections for instrumental backgrounds, detector efficiency and sample transmission, the scattered intensities were normalized to a constant sample thickness and incident beam flux. The normalized intensities were further converted to the absolute scale, in units of cm^{-1}, by means of precalibrated secondary standards[8].

RESULTS AND DISCUSSION

The stress–strain relation of the PED/PEH blend is given in *Figure 1*. Although the yield point can be readily discerned in this figure, there is no drop in stress as is commonly observed in the tensile stress–strain curves of polyethylene of similar molecular weight. This absence of yield drop is likely to be a consequence of the deformation mode used in this work; a uniform strain was forced upon the whole sample and the necking of the sample was suppressed. Nevertheless the result of *Figure 1* clearly shows that the blend starts to undergo plastic flow after a strain of ~20%. The contribution of friction between the sample and the steel die was not excluded and therefore the stress levels shown in *Figure 1* represent the upper limits of the true values.

For segregated polymer blends, the scattered intensities have been modelled in terms of a correlation function of $e^{-r/\xi}$ with modest success[7]. Here ξ denotes the correlation length. Accordingly, one expects the square root of the inverse of the intensities, $I(q)^{-1/2}$, to vary as a function of q^2. The result of the undeformed sample was plotted as $I(q)^{-1/2}$ *versus* q^2 (*Figure 2*), and a quadratic fit (solid line) through the data points was used to locate $I(0)$. The range for fitting was 0.0033 Å$^{-1} < q < 0.015$ Å^{-1}. The $I(0)$ for the undeformed sample was found to be 2528 cm^{-1}. For a homogeneous blend with 4 vol% PED and a molecular weight of ~150000 the corresponding value is 70.9 cm^{-1}. The above experimental result demonstrates that the blend is indeed highly segregated.

A total of 13 deformed samples at different strains were prepared. The extrapolated values of $I(0)$ *versus* strain

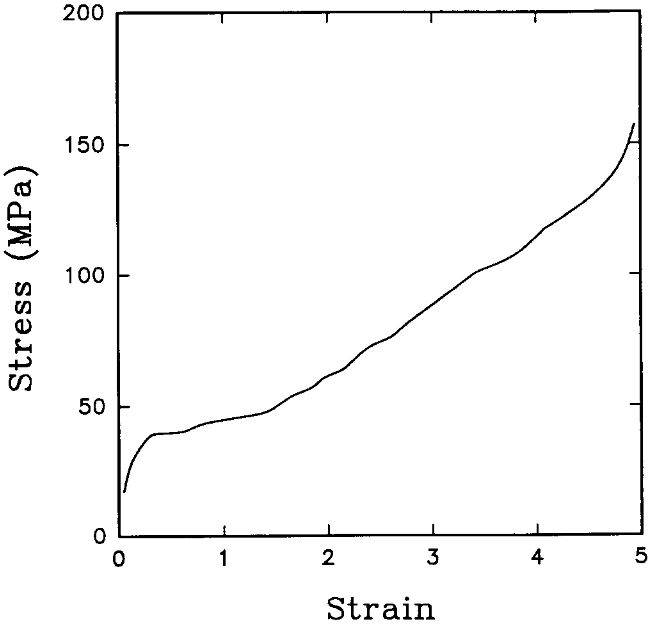

Figure 1 The stress–strain curve of the PEH/PED blends deformed at room temperature in a pure shear mode

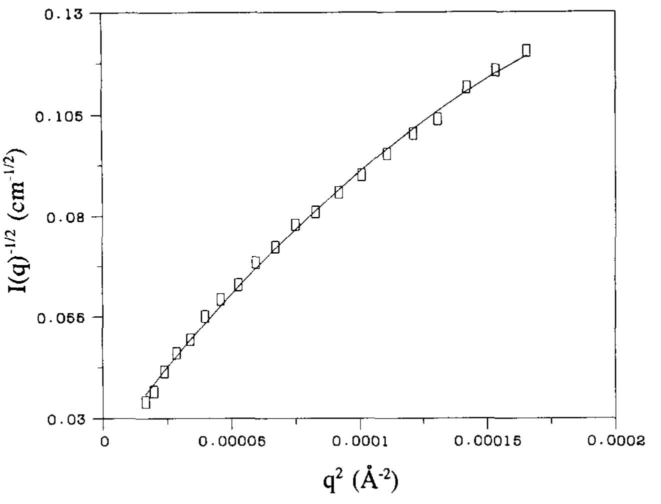

Figure 2 SANS result of the undeformed PED/PEH sample. The solid line represents the best fit through the data points to determine the zero angle intensity

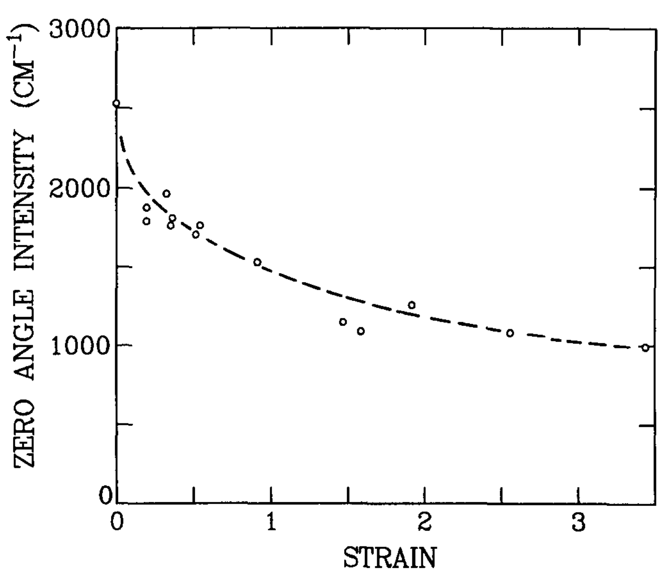

Figure 3 Zero angle intensities of one undeformed PED/PEH blend and 13 others deformed to different strains. The dashed line is simply a guide to the eye. All the data were obtained with a sample to detector distance of 19 m

are given in *Figure 3*. The abrupt drop of $I(0)$ around the strain of 0.2, corresponding to the yield point, is very striking. Unfortunately, we were unable to prepare any plastically deformed samples with strain below 0.2; a complete recovery took place in samples deformed near the yield point. Beyond the yield point, $I(0)$ exhibits a modest decrease with the plastic strain. In our earlier work, the value of $I(0)$ decreased by a factor of five, which is higher than observed in this work. However, the samples in the previous study were deformed by a strain of 13 which is much higher than employed here.

We now focus attention on the connection between our experimental findings (*Figure 3*) and the deformation mechanisms mentioned in the foregoing section. Based on the dislocation mechanism, the generation of screw dislocations and the onset of their movement mark the yield point. The slip distance, or the magnitude of its Burgers vector, was proposed to be one C–C bond length. With the deformation scheme used in this work, the macroscopic slip directions are along $(1, 0, -1)$ and the equivalent ones. One expects that the majority of the dislocations has the Burgers vector parallel to these directions. These dislocations will contribute very little to the disturbance or the displacement of chains along the $(0, 1, 0)$ direction. It is noteworthy that all our SANS data were collected along this axis $(0, 1, 0)$. The only processes causing significant displacement of chains along $(0, 1, 0)$ are those which can lead to a reduction in $I(0)$. Therefore, the current SANS result would preclude any pure mechanical model as the sole process for yielding and the subsequent plastic flow in semicrystalline polymers. In addition to the SANS results, recent force–length measurements have shown that for random ethylene copolymers[9], as well as for linear polyethylene[10] the reduced yield stress is not altered with changes in the crystallite thickness in the chain directions. These findings are contrary to the theoretical expectation from the dislocation theory[4,5].

In contrast, for the partial melting–recrystallization mechanism, there is no restriction in the direction of chain diffusion within the local molten zone. In other words, even though the local melting is caused by a pure shear process with the slip direction along $(1, 0, -1)$, randomization of the partially segregated PED chain is expected to occur in all directions including $(0, 1, 0)$. Hence the decrease in $I(0)$ at the yield point can be taken as evidence for partial melting.

The rapid decrease in $I(0)$ at the yield point also needs to be examined. For the dislocation model, the reduction in $I(0)$ should change gradually with plastic strain. For the partial melting and recrystallization model, one might expect that the extent of $I(0)$ reduction could be related to the amount of energy input into the sample. The abscissa of *Figure 1* registers the instant total strain including the viscoelastic and the plastic components whereas the abscissa of *Figure 3* represents the plastic strain. According to *Figure 1*, the amount of elastic strain up to the yield point is about 0.2. This strain needs to be added to the plastic strain of *Figure 3*. In other words, the total strain of the first data point at a plastic strain of 0.197 is 0.397, denoted as ε_1. The total work input to this sample is roughly $1/2\sigma_y 0.2 + \sigma_f 0.197$. For all the other post-yield samples, the additional work input is about $\sigma_f \delta\varepsilon$ where $\delta\varepsilon$ is the strain increment beyond ε_1, σ_f and σ_y denote the flow stress and the yield stress, respectively. In the region of strain less than 1.0 the magnitudes of σ_f and σ_y are about the same. According to the above argument, if the drop in $I(0)$ in *Figure 3* is due solely to the elastic energy term it should be equal to $1/2\sigma_y 0.2$. However, the observed decrease is too large to be explained solely by the contribution of the elastic energy term. The decrease in molecular weight at the yield point, as manifested by the drop in $I(0)$, does not need to be directly proportional to the amount of partial melting, or the elastic energy absorbed. There can easily be a magnification effect.

The isotopic segregation signal was also used as an indicator of the melting and recrystallization mechanism by Sadler and Barham (SB), in studies[11–13] of drawing and necking of polyethylene fibres. In contrast to the experiments described in this work, most of the undeformed samples were prepared with a statistical distribution of labelled molecules. The appearance of excess scattering was taken to indicate that local melting and recrystallization had been produced by deformation, thus allowing sufficient molecular mobility to segregate.

Such effects, which were seen at drawing temperatures of ~70–90°C, were interpreted in terms of melting and recrystallization produced by deformation and this is consistent with the conclusions drawn from this work. There is, however, a significant difference in interpretation of the data at lower draw temperatures. It was recognized that no excess scattering is expected if the melting and recrystallization occurs in such a fashion that the molecules are effectively quench-cooled and hence have insufficient time and/or mobility to segregate. Thus it is well known that PEH/PED blends do not exhibit a segregation signal when rapidly quenched from the melt. Thus, SB also prepared[11] initially segregated samples and measured the SANS cross section as a function of deformation. As in this work, the decrease in the excess M_w or R_g would provide strong indirect evidence of melting and recrystallization and it was shown that deformation produced a reduction in R_g by a factor of 1.7–2.1 in the temperature range 20–64°C. We would interpret such changes as evidence for a melting and recrystallization mechanism, though SB assigned them to 'the finite instrumental resolution'. SB were the first to point out the necessity of allowing for such effects in SANS studies of oriented polymers[14] which occur when the molecular dimensions exceed the resolution limit of the SANS instrument. However, as demonstrated by one of us[15], the finite resolution of the instrument affects only $I(0)$ (and hence M_w) and not R_g. The latter parameter, measured perpendicular to the draw direction, actually becomes smaller, and hence easier to resolve, as the molecules shrink perpendicular to the draw direction. Thus resolution effects cannot cause a decrease by the factor ~2 in R_g, as observed by SB. Such a decrease is easily explained in terms of melting and recrystallization and we are of the opinion that this is the underlying cause of the changes in both M_w and R_g as observed by SB and ourselves.

In summary, the SANS results show that $I(0)$, intensities extrapolated to zero angle, start to decrease at the onset of plastic deformation. A rapid decrease in $I(0)$ takes place just beyond the yield point. Thereafter, the decrease in $I(0)$ follows smoothly with the plastic strain. Since the SANS data were collected along the axis with the strain component equal to zero, the dislocation model, or any other pure mechanical ones, have difficulty in accommodating this observation. As to the partial melting and recrystallization model, since the diffuse direction of the chain within the local molten zone can be random, the decrease in $I(0)$ can be interpreted qualitatively. It represents a decrease in the molecular weight of the deuterated species as a consequence of partial melting and crystallization. This process can be taken to be a major contribution to yielding.

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