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A small-angle neutron scattering study of the plastic deformation of linear polyethylene

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Small-angle neutron scattering (SANS) studies of a 5 vol% mixture of deuterated linear polyethylene with a protonated one was used to investigate the role of partial melting–recrystallization during the solid-state deformation of the polymer in pure shear. The extension of previous studies now gives data that cover the complete deformation range in a continuous manner. The quantity R_0, the ratio of the scattering at zero angle for a given strain to that at zero strain, decreases very rapidly in the strain range 0–2. Here only modest changes occur in the stress–strain curve. In the deformation region where the stress increases rapidly with strain, only a relatively small decrease occurs in R_0. The SANS results indicate that the major reorganization and homogenization occur at low strain. These results, coupled with the Flory–Yoon hypothesis of partial melting–recrystallization, explain the observations that for a ductile-type deformation the ultimate properties do not depend on the structural factors that define the initial undeformed state.

(Keywords: small-angle neutron scattering; plastic deformation; polyethylene)

INTRODUCTION

The mechanical properties of polymers in general, and semicrystalline ones in particular, are of primary importance in determining their end uses. The development of a molecular understanding of the deformation of crystalline polymers is thus important and has been an arduous task over a long time period[1–7]. The difficulties that have been encountered are essentially due to the multiphase structure of such systems, the inherent continuity of long-chain molecules and their trajectory through the different regions. Typically, a given polymer molecule will pass through the ordered crystalline region, the liquid-like region and the interphase that connects them[8,9]. Delineating the trajectory of such a chain is thus crucial to the understanding of properties. The analysis is complicated further by the major changes that occur in the character of the stress–strain curves, and in the key tensile parameters, by variations in the molecular constitution of the polymer molecules and in alterations of the key structural parameters that describe the crystalline state[10].

In essence, the total problem of interest, stated in terms of a uniaxial or tensile-type deformation, is how an initial set of randomly arranged, anisotropic crystallites are transformed into a highly axially oriented fibrillar system. Two quite different approaches have been made in analysing the problem. One is rooted in the knowledge gained from long-standing studies of the deformation of metals[5–7,11,12]. The focus in this case is directed virtually entirely to the changes that occur in the crystalline region during deformation. The other approach takes cognizance of the total phase structure of the polymeric system. It is based on a partial melting–recrystallization process[13,14] and on the influence of the non-crystalline regions on the deformation.

Small-angle neutron scattering (SANS) studies have made important contributions to the resolution of this problem[15–17]. Because the radius of gyration (R_g) of polymer molecules is virtually unchanged on crystallization[18,19], the chains have a similar distribution of mass elements in the solid and melt states. Thus, the entanglements which exist in the melt must be duplicated in the solid state. This implies that the interconnections between neighbouring crystallites preclude relative movement without their destruction. Flory and Yoon[13] used these considerations to argue that the crystalline regions must melt and recrystallize during the deformation process. Wignall and Wu[15,16] made use of a segregation artefact to test this hypothesis. SANS studies of melt crystallized blends of deuterated (PED) and protonated (PEH) polyethylenes have shown that correlated aggregates or paraclusters[20] of PED molecules in PEH are created by slow cooling the melt in the region

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(135–125°C). This gives rise to an anomalous SANS signal or excess 'molecular weight', which is unaffected by annealing outside the melting region, but can be eliminated by melting and quenching the sample. The basic idea of the experiments was to apply solid-state deformation to a mixed PEH/PED blend in temperature ranges where the annealing alone is known not to affect the SANS signal. Large reductions in intensity (or M_w) were observed[15–17] and gave strong support to the partial melting–recrystallization hypothesis of Flory and Yoon[13]. These conclusions were based on a model of clustering[20], where the chain trajectories and centres of mass were only slightly perturbed from a random distribution of molecules. Alternatively, the excess intensities have been attributed[21] to domains in which the average concentration of the D-labelled molecules is enhanced or depleted over much longer length scales. It should be noticed that such a hypothesis would only reinforce the conclusions based on the paracluster model[20]. If small perturbations of the molecular configuration cannot be randomized without local melting and recrystallization, then the removal of large-scale perturbations, involving molecular transport over distances large compared with the R_g, is even more dependent on this mechanism. Thus the conclusions drawn from the SANS studies of solid-state deformation are independent of the particular model chosen to interpret the excess SANS intensities.

In this work we extend the earlier studies[15–17] by analysing the SANS in a step-wise manner over the complete deformation range. In this way a more detailed comparison of the SANS results can be made with the deformation studies.

EXPERIMENTAL

The experimental procedures adapted here are very similar to those used previously[15,17]. Samples containing 5% deuterated linear polyethylene ($M_w = 95\,000$, $M_N = 17\,560$) in a matrix of 95% protonated linear polyethylene ($M_w = 106\,000$, $M_N = 9000$) were blended in dichlorobenzene, precipitated in methanol, then filtered and dried. The material was then held at ~160°C under vacuum, pressed into slabs and cooled at a rate of 3–4°C min^{-1}. This crystallization procedure results in a segregated system[15,22]. Samples with initial thickness >2 mm were made up from slabs 1 to 2 mm thick with densities of 0.95 g cm^{-3}.

The deformation was performed in a set of matched dies as described in earlier work[15,17]. The compression was produced by an Instron electromechanical test system operating at room temperature. The mode of deformation was pure shear. Samples were elongated along the x-axis and compressed along the z-axis while the dimension along the y-axis remained constant. The strain was taken to be the ratio of the change in sample thickness. The thicknesses were determined a few days after the load was released to allow for the recovery of elastic or viscoelastic strain. Hence, the strain reported with the SANS results is the plastic strain. An initial strain rate of 0.01 s^{-1} was used for all samples. The stress was calculated as the compression load divided by the instantaneous cross-sectional area of the samples. The contribution of friction between the sample and the steel die was not excluded and therefore the stress levels reported represent the upper limits of the true values. An effort was made to mitigate this effect through the use of a mould-release coating on the die surfaces. The stress–strain behaviour of the slowly cooled blend is shown in *Figure 1*. No deformation occurs along the principal y strain axis. Hence, the SANS intensities of the deformed samples were taken along this axis.

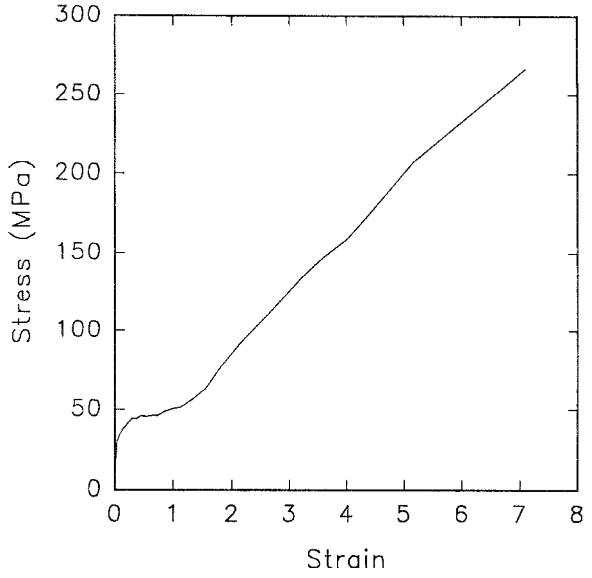

Figure 1 Room temperature stress–strain curve of a PEH/PED blend deformed in a pure shear mode

SANS data were obtained over a range of momentum transfer $0.04 < Q < 0.35\,\mathrm{nm}^{-1}$ on the 30 m instrument at the W. C. Koehler small-angle scattering facility of Oak Ridge National Laboratory. Q is defined as $(4\pi/\lambda)\sin(\theta/2)$, where λ, the neutron wavelength, was 0.475 nm ($\Delta\lambda/\lambda = 0.06$) and θ is the scattering angle. For the undeformed sample, the two-dimensional scattering patterns were circularly averaged to yield an intensity *versus* Q plot. For the deformed samples, intensity slices of the pattern were taken along the axis of zero strain (y-axis). After corrections for instrumental backgrounds, detector efficiency and sample transmission, the scattered intensities were normalized to a constant incident beam flux and unit sample volume. The normalized intensities were then converted to an absolute differential cross-section, per unit solid angle, per unit sample volume (in units of cm^{-1}), by means of secondary standards[23].

As in ref. 17, a quadratic fit to $I(Q)^{-1/2}$ was used to determine the value $I(0)$. Examples for $\epsilon = 0$ and 9.6 are shown in *Figure 2*. A correction for the H^1 incoherent background (~1 cm^{-1}) was also applied as in the former studies[15,17], though this caused only a minor perturbation to the data.

RESULTS AND DISCUSSION

The stress–strain relation of the PED/PEH blend is shown in *Figure 1*. This type of curve is expected for this molecular weight linear polyethylene, crystallized in the manner described[11]. Characteristically, yielding occurs at a strain of ~0.2. The stress remains essentially invariant with strain up to a strain of ~1.2. As the strain increases above this value, there is a continuous increase, or upsweep, in the stress.

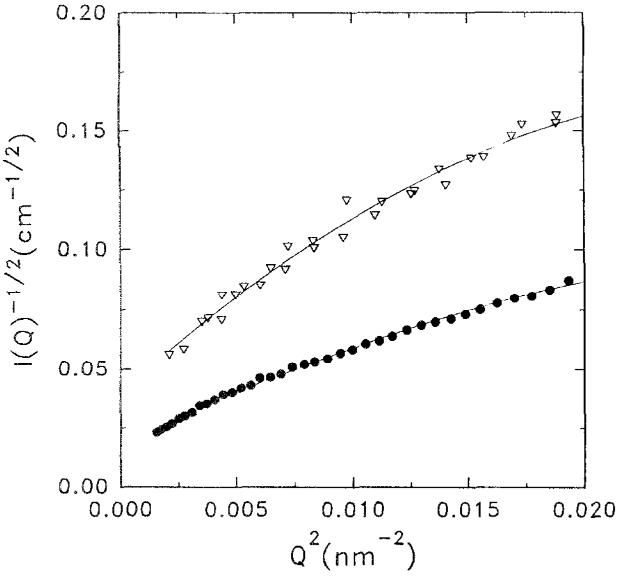

Figure 2 Intensity I versus Q: ●, undeformed sample; ▽, deformed sample, strain = 9.6. Solid lines are for a quadratic fit to the data

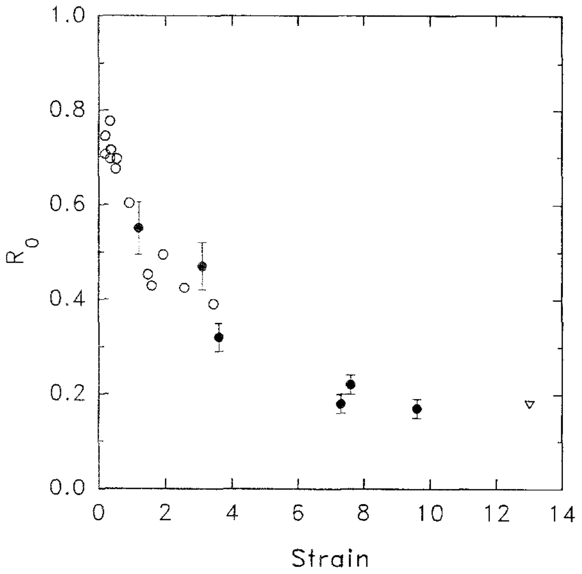

Figure 3 Summary of PEH/PED blend deformations. R_0 is the ratio of $I(0)$ at zero deformation to $I(0)$ at the appropriate value of the strain. ●, Present work; ○, ref. 17; ▽, ref. 15

Typical examples of $I(Q)^{-1/2}$ against Q^2 are given in *Figure 2* for both an undeformed specimen and a slice along the zero strain axis for a sample with a strain of 9.6. The average value of the differential scattering cross-section at zero angle, $I(0)$, for three different undeformed samples is $3500 \pm 100\,\mathrm{cm}^{-1}$. The expected value based on a completely random distribution of the PED molecules is $\simeq 51\,\mathrm{cm}^{-1}$. Subsequent deformation to the highest strains results in a five- to sixfold decrease in $I(0)$, which suggests that complete homogenization does not occur.

More detailed results of the deformation experiments, as well as the data from earlier works, are summarized in *Figure 3*. Here the ratio R_0 of the scattering intensity of the deformed sample at a strain of ϵ at zero angle, $I_\epsilon(0)$, to that of the undeformed sample at zero angle, $I(0)$, is plotted as a function of strain. The new data points fit smoothly in line with the results of the earlier reports[15,17]. Previously the scattering data were only available at a strain of ~13 (ref. 16), corresponding to fracture, and at the low values of strain[17]. The gap in the data has now been removed by the new results.

In examining the data in *Figure 3* we note that there is a very rapid decrease in R_0 in the strain range of 0–2. The further decrease in R_0 with strain is fairly modest. It becomes essentially constant from a strain of ~5 until failure. There is a five- to sixfold decrease in R_0 over the complete deformation range, with the major changes occurring at strains of <2. This decrease in intensity is a reflection of the concomitant decrease in apparent molecular weight. Hence these results support the previous conclusion that the true molecular weight is being approached with deformation. As the clustering of the units is minimized the sample in turn becomes homogeneous with respect to the two species. It has been shown[16,17] that the anomalous intensities of SANS M_w arise from an excess of nearest neighbour contacts between PED chain units above that which would be expected purely on a random statistical basis. However, as noted above, other models of the excess SANS intensities[21] would lead to similar conclusions.

It is of interest to compare the changes in R_0 with strain with the stress–strain curve of *Figure 1*. As we have noted, there is a rapid decrease in R_0 to a strain of ~2. This observation encompasses the yield point and correlates quite well with the very modest change in stress with strain that occurs in this region. Most of the homogenization of the species has, however, taken place in this deformation region. In contrast, when a large and continuous increase in the stress with strain is observed in *Figure 1*, only a very modest decrease in R_0 occurs. Thus, the major homogenization of the system takes place at relatively small strains from the yield point to extension ratios ≈1.2. Similar studies could not be carried out at strains below yield because of recovery of the sample.

The local reorganization that is mandated by the SANS results can be readily explained by the Flory–Yoon hypothesis of a partial melting–recrystallization mechanism. Details of this concept have been discussed in detail elsewhere[10,13,15,17]. It is worthy of noting again, however, that raising the temperature is not a requirement for partial melting to take place. Neither does complete melting have to occur. The applied stress will cause the melting of the less perfect crystallites, and recrystallization will follow during the deformation.

The SANS results, coupled with the Flory–Yoon hypothesis, explain in a straightforward manner the earlier observations that in a plastic or ductile deformation, the ultimate properties do not depend on the initial structural factors that describe the undeformed crystalline state[10,24]. Peterlin and co-workers have also shown that the long spacing of the final fibrillar system depends only on the deformation temperature and not on the initial spacings[25,26]. The reorganization and homogenization of the system at low strain, as deduced from the SANS results, explains the independence of the intial structure.

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