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Deformation of oriented polyethylene - additional effects observed at high temperatures

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This paper serves to overcome an apparent contradiction in the literature on the subject of deformation of polyethylene with simple lamellar textures, in particular on the observation of strains which are larger than would follow from the accompanying changes in texture when deformation is carried out at elevated temperatures. It is shown that if both the strain and texture determination are carried out at the temperature of deformation (and not after cooling), previous contradictions are eliminated and all the observed effects can be explained by temperature-dependent structural processes known to take place from evidence without the need to invoke *ad hoc* assumptions regarding the structure.

1. Introduction

Low-density polyethylene in "double texture" or "single texture" form has been the subject of extensive investigation concerning its deformation behaviour [1, 2]. The emphasis has been on relating changes in sample dimension to changes in lamellar periodicity as determined by low-angle X-ray diffraction, further analysis of the changes in lamellar and chain orientation enabling the actual deformation processes to be identified and their relative contributions quantified. A principal finding of this work has been that when a sample is extended or compressed, the percentage change in sample length is equal to the percentage change in the lamellar periodicity projected on the same direction. This is consistent with the sample being composed entirely of stacks of lamellae arranged with their axes along the direction of the drawing process used to prepare them.

However, this result appears to conflict with preceding work partly carried out in this laboratory [3, 4] which showed that the change in sample length was greater, by a factor of between two and three, than could be accounted for by the lamellar deformation. This led to the suggestion that the samples contained a structural element in addition to the lamellae monitored by X-ray diffraction, and that this component was responsible for the excess dimension changes. The purpose of this paper is to reconcile these two sets of observations. While it also presents new information of interest in its own right, an appreciation of the contradiction it sets out to remove and a certain amount of familiarity with the material in [1–4] is presupposed.

The principal difference between the two groups of studies is that in the experiments in which equality was found between changes in microscopic and macroscopic parameters, diffraction patterns were recorded at the temperature at which the sample was strained (usually, but not always, room temperature), whereas in the earlier experiments deformation was carried out at high temperatures within the melting range of the samples, but diffraction patterns were only recorded at room temperature. It will be shown that the "excess dimensional changes" observed in the latter case can be attributed to two distinct processes. Compression of lightly annealed samples at high temperatures produces irreversible shrinkage, together with specific texture changes, suggesting that a reorganization of the structure takes place similar to that which occurs on annealing. In more highly annealed samples the

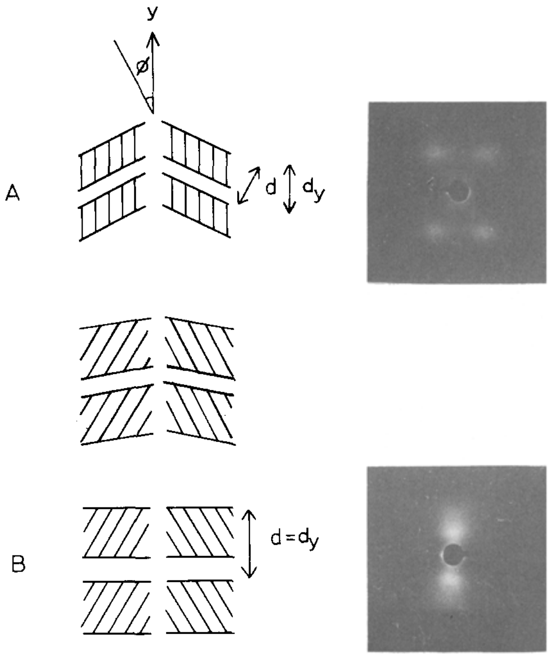

Figure 1 Change in lamellar texture with increase in annealing temperature as deduced from low- and wide-angle X-ray diffraction patterns. Sample type A corresponds to annealing at 85° C, B to 100° C. (The sketch in the middle serves to illustrate the continuous transition between the two.) Low angle X-ray diffraction patterns correspond to sketches A (four points) and B (two points).

excess dimension changes are related to the temperature-reversible changes in long spacing which have recently been explained in terms of partial melting [5].

2. Experimental

The two principal texture types used are illustrated in Fig. 1 together with corresponding low-angle diffraction patterns. The samples were prepared by drawing, rolling and annealing at different temperatures, in this case 85° C (sample type A) and 100° C (sample type B). We are concerned with the relationship between the percentage change in sample length y and in lamellar periodicity d_y. These will be denoted Δy and Δd_y respectively, in accordance with the convention used in [1] (although not in [2]). As $d_y = d/\cos\phi$ where ϕ is the angle made by the lamellar normal with y, a change in d_y can be caused by a change either in ϕ or in d which, in turn, can be caused by changes in chain obliquity or in lamellar separation. The interpretation of these changes in terms of lamellar slip, chain slip and lamellar separation has been discussed in detail elsewhere [1, 2] and will not concern us here.

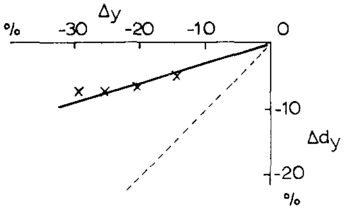

Figure 2 Relationship between Δd_y and Δy on compressing a type A sample at 85° C.

Experiments were carried out by extending or compressing samples inside an oven mounted on a Rigaku-Denki low-angle X-ray diffraction camera. Diffraction patterns were recorded at room temperature before deformation, at elevated temperature before and after deformation, and at room temperature after cooling at constant length.

3. Results and discussion

3.1. Type A samples

Fig. 2 shows the results of compressing a sample of type A at its annealing temperature of 85° C, Δd_y being obtained by comparing lowangle diffraction patterns recorded at 85° C before and after defromation. These results show that $\Delta y \sim 3 \times \Delta d_y$, i.e. only a third of the change in sample length can be accounted for by the lamellar deformation, in agreement with results obtained by comparing diffraction patterns recorded at room temperature [3, 4]. In these samples the changes in the low-angle diffraction pattern on heating or cooling are small.

Further information was obtained by releasing the stress at 85° C. As shown in Table I the lamellar periodicity recovered its initial value, accompanied by a corresponding increase in

TABLE I The effect on d_y and d of compressing a type A sample at 85° C, removing the stress at 85° C, then cooling

Temperature (° C)	Δy (%)	Δd_y (%)	$\Delta y - \Delta d_y$ (%)	Δd (%)	θ°
RT	0	0	0	0	30
85	0	0	0	0	26
85	−27	−10	−17	0	12
85 (relaxed)	−18	0	−18	+10	12
RT	−18	0	−18	+10	16

sample length. Thus the excess dimensional changes are irreversible.

It can also be seen that the recovery in d_y is caused by an increase in the actual long spacing d rather than by reversing the change in ϕ caused by the compression. Thus the net result of the deformation has been to increase d and decrease ϕ such that $d_y = d/\cos\phi$ remains approximately constant, and to produce an irreversible shrinkage of the specimen. These changes are very similar to those which would be expected on annealing the undeformed sample at a higher temperature, leading from type A samples towards type B samples. Thus it appears that compression at a given high temperature promotes the texture changes and sample shrinkage which would normally occur on annealing at a somewhat higher temperature. The effects were only observed at temperatures of 80° C or above, the temperature range in which annealing effects occur. They were also observed in samples annealed at 90° C and to a lesser extent in samples annealed at 100° C. In more highly annealed samples the scope for compression-induced shrinkage would be expected to be reduced, and another effect predominates as described in the next section.

3.2. Type B samples

When type B samples are heated to their annealing temperature a temperature-reversible change in long spacing of about 20% is observed. In these samples different relationships between Δd_y and Δ_y are obtained on deformation at high temperatures depending on whether X-ray diffraction patterns taken at room temperature or at high temperature are compared. This is illustrated in Figs. 3 and 4 for samples compressed and extended at 100° C. The figures show the effect on d_y of (1) heating to the deformation temperature, (2) deforming by an amount Δy, (3) cooling at constant length. It can be seen that in both cases the difference between Δy and Δd_y is much larger at room temperature than at high temperature, the difference arising from the fact that the change in d_y on cooling is different from the change in d_y on heating.

In both cases the orientation changes on heating and cooling were small so we are concerned essentially with changes in long spacing d which occur at constant sample length. It has recently been suggested that the reversible change in d with temperature is caused by melting and recrystallization of small lamellae within the lamellar stacks which alters the average lamellar periodicity [5]. Thus it is reasonable to suppose that straining the sample would affect this process. The small decrease in long spacing on cooling samples under compression, indicated by the dotted line in Fig. 3, may be a result of deformation or displacement of the molten material to the extent that it does not recrystallize into lamellar form. On the other hand, extension may facilitate crystallization of molten regions on cooling so that many additional thin lamellae are formed between existing ones, leading to the large decrease in long spacing on cooling shown in Fig. 4.

3.3. High-density polyethylene

Experiments have been carried out on similar samples of high-density polyethylene by compressing them at 128° C [6]. No excess dimensional changes were observed and this was interpreted as an indication that the high-density samples do not contain the structural component responsible for them in low-density samples. According to our interpretation, large excess dimensional changes would not be expected in

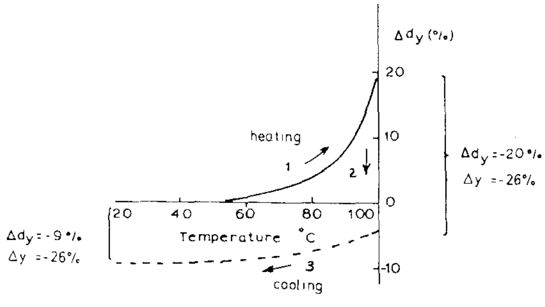

Figure 3 Diagram to show the change in d_y relative to its initial value at room temperature, on heating to 100° C, compressing at 100° C, then cooling at constant length.

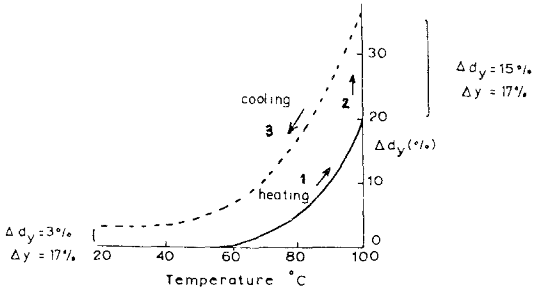

Figure 4 Diagram to show the changes in d_y which occur on heating to 100° C, extending at 100° C, then cooling at constant length.

high-density polyethylene as the reversible change in long spacing is small (~10%). One could suppose that some excess dimensional changes might arise in compression due to the mechanism associated with annealing. However, this is not likely to apply to the present samples as these were already highly annealed and were deformed somewhat below their annealing temperature. Thus any difference in behaviour between high- and low-density material is a manifestation of the greater degree of disorder within the lamellar stacks in the latter, which leads to the wide melting and annealing range and to the large temperature-reversible changes in long spacing; there is no need to invoke any structural unit in addition to the lamellar stacks.

4. Conclusions

There thus seem to be two distinct reasons why large "excess dimensional changes" may be observed when oriented polyethylene samples are deformed at temperatures within the melting range. First, on compression the samples are enabled to continue the irreversible reorganization process, such as is responsible for shrinkage in annealing experiments, hence correspondence between y and d_y is lost; indeed there is no correspondence between changes in long spacing and sample dimension in the usual annealing experiments on fibres or single crystal mats. Second, if the deformation temperature is within the range in which large reversible changes in long spacing are observed, different results are obtained depending on whether observations are made at the deformation temperature or at room temperature, an effect closely related to the reversible spacing changes attributed to partial melting. Failure to recognize this can result in erroneous correlation between sample size and long spacing producing the apparent contradiction in past works on the subject.

Acknowledgements

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