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Plastic deformation of linear polyethylene containing row structures

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The mechanical and thermal properties of highly oriented polyethylene films containing "shish kebab" type morphology are studied. At low deformations (strain $\epsilon < 10\%$) strong work hardening is observed. Higher deformations ($\epsilon > 40\%$) give rise to strain softening of the material and a decrease in the Young's modulus of as much as one-third of its initial value. In addition, the high melting component of the material originating from the shish-type crystals vanishes on higher deformation. The deformation processes are discussed from the point of view of a fibre-composite material and structural changes during the deformation are followed by transmission electron microscopy.

1. Introduction

The plastic deformation of polymeric solids containing row structures [1–4] can be described in terms of a fibre reinforced material [5–9]. In these materials needle-like extended chain crystals having high Young's modulus are embedded in a low modulus matrix. The low modulus matrix may either be composed of amorphous polymers or a matrix of amorphous and lamellar crystallized material. Several models have been proposed in order to explain the stress–strain properties in the elastic as well as in the plastic region [3–13]. However, the lack of morphological informations is a most severe obstacle in testing the various proposed models.

Recently, a new method has been developed by which highly oriented thin films of polymers can be obtained [4]. The single films are transmissible in the transmission electron microscope (TEM) and the structure of the films can be determined without any further modification of the film by the phase contrast electron microscopic technique. Sandwich layers of these films can be used for the measurements of thermal and mechanical properties [14]. It is the purpose of this paper to present a direct correlation between the microstructures and mechanical and thermal properties of these materials.

2. Experimental procedure

The polyethylene utilized in the present studies was obtained from BASF (Lupolen-5261Z having a molecular weight, $\bar{M}_w = 3.5 \times 10^5$). Highly oriented crystalline films of polyethylene were prepared under very high longitudinal flow gradients ($\approx 4 \times 10^4\,\text{sec}^{-1}$) by the method of Petermann and Gohil [4]. For the structural characterization, a JEM 200 A electron microscope operated at 100 kV was used. Thermal characterizations of samples were carried out on a Perkin-Elmer-DSC-II. Mechanical tests were performed using a conventional Instron machine in which the straining rate for all samples was kept constant ($0.03\,\text{min}^{-1}$). The crystalline orientation of the strained material was recorded by wide-angle X-ray diffraction.

3. Results

Fig. 1 shows a phase contrast electron micrograph of a polyethylene film crystallized under high longitudinal flow conditions. The high degree of orientation is evident from the electron diffraction pattern shown in the inset. The morphology revealed from the electron micrograph is of a shish kebab type. The central shish or core structure (needle-like crystals) becomes more apparent when the lamellar crystals are melted.

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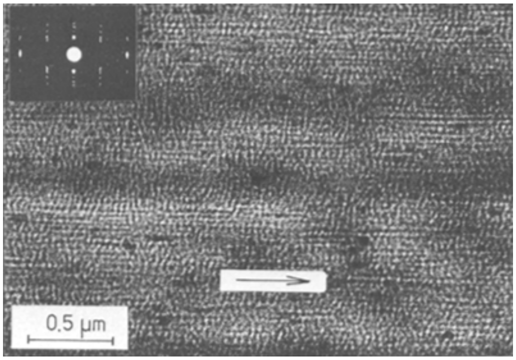

Figure 1 Phase contrast electron micrograph of a polyethylene film. The arrow indicates the molecular direction. The electron diffraction pattern shows the high molecular orientation in the crystals.

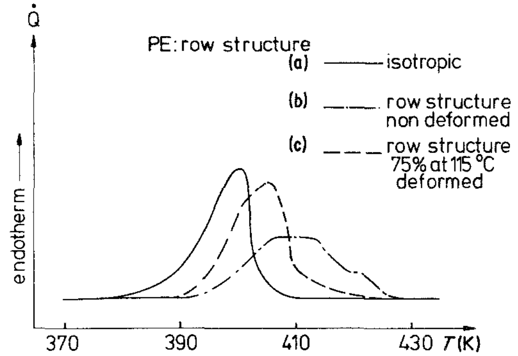

Figure 3 DSC scans of polyethylene films: (a) isotropic sample, (b) non-deformed oriented film and (c) 75% deformed oriented film.

Fig. 2 is a phase contrast electron micrograph of a film taken at 137° C where the lamellar type crystals of the shish kebab morphology is melted, and indicates clearly the presence of needle-like crystals. The morphology of the film can be described as a composite structure consisting of stiff needle-like crystals embedded in a softer matrix of lamellar crystals and amorphous material. The concentration of the needle-like crystals determined from the differential scanning calorimetry (DSC) traces is nearly 30%. The presence of the needle-like crystals (high melting component) is seen in DSC scans; needle-like crystals start melting at about 142° C and some of them are thermally stable up to 155° C. For a comparison, a DSC scan of isotropic polyethylene (PE) is also shown in Fig. 3. It can be concluded from the heating experiment shown in Fig. 4 that the high melting temperatures are not due to a superheating effect. Three samples were annealed at 414 K for various times at constant strain. In each case the heat flow indicated by the DSC has been normalized for sample mass and sensitivity of the apparatus. Subsequently, DSC scans were taken and no change in the high temperature part of the curve could be detected.

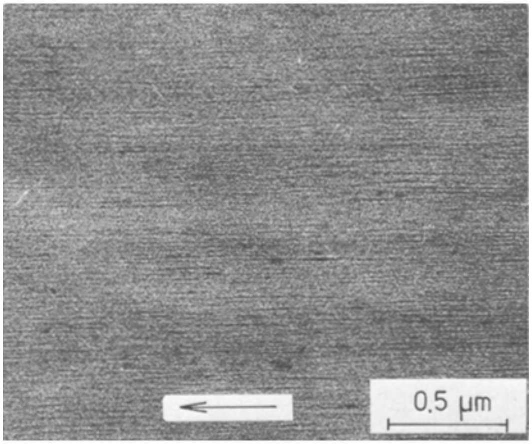

Figure 2 Phase contrast electron micrograph of a polyethylene film taken at 137° C. Note the presence of only needle-like crystals. An arrow indicates the molecular direction.

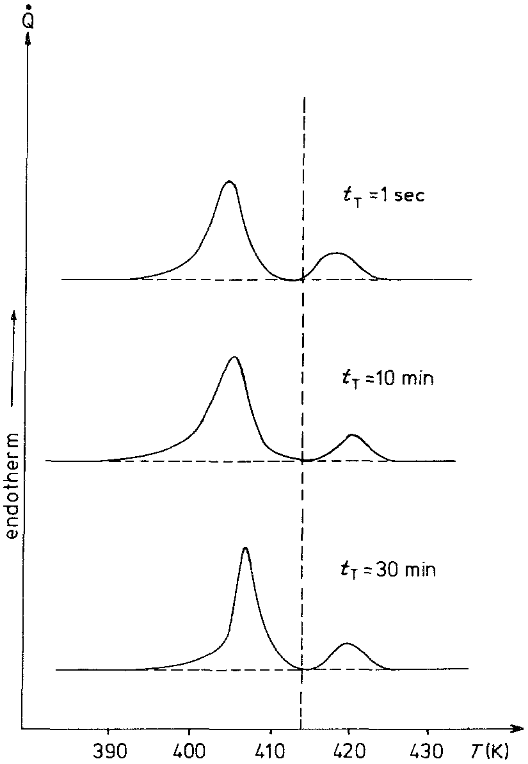

Figure 4 DSC scans of three oriented polyethylene samples. The samples were held at 414 K for indicated periods of time (t_T) and then scanned further.

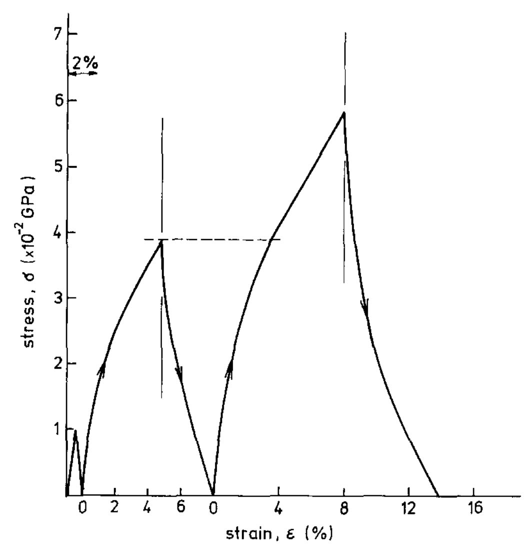

Figure 5 Stress–strain cycles for a polyethylene sample. Strain rate is $\dot{\epsilon} = 0.03\,\text{min}^{-1}$.

Fig. 5 shows stress–strain cycles of a PE film taken at room temperature. In the first cycle, the sample is strained by 0.5% and the straining is completely reversible (elastic). In the second cycle, the sample is strained by 4.8% and released again. After the initial elastic region (0.8%), plastic flow with high work hardening starts. The Young's modulus and work hardening coefficients $d\sigma/d\epsilon$ are functions of temperature (where σ is stress and ϵ is strain). With increasing temperature, the Young's modulus as well as the work hardening coefficient drops. The fracture strain increases with increasing temperature from 8% at −196° C to nearly 100% at 115° C. Fig. 6 shows a stress–strain curve of a PE film taken at 115° C. Most surprisingly a strain softening ($d\sigma/d\epsilon < 0$) for strains higher than 40% can be observed. The sample deforms homogeneously and X-ray photographs do not show any change in the orientation of the crystals.

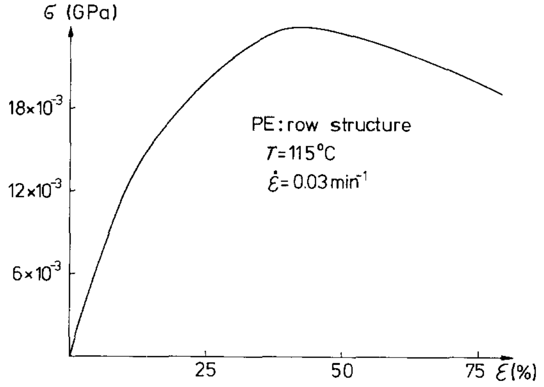

Figure 6 Stress–strain curve of a polyethylene sample taken at 115° C. The strain rate is $\dot{\epsilon} = 0.03\,\text{min}^{-1}$. Note the strain softening behaviour at higher deformation.

In order to examine the effect of the straining on Young's modulus E, three samples were deformed at 95° C for 30, 65 and 75%, and subsequently their Young's modulus were measured at − 196° C (Table I). The Young's modulus E decreases from 20 GPa for an undrawn sample to 12.4 GPa for a sample strained by 75%. A similar experiment has been performed in which the samples were deformed by the same amount but the deformation temperature was varied ($\epsilon = 67\%$, $T = 80$, 95 and 115° C). The Young's moduli of these samples, taken subsequently at − 196° C, are shown in Table I. Again, a continuous drop in Young's modulus from 20 to 6 GPa for the sample with the highest deformation temperature is evident. The DSC scan of strained samples (Fig. 3) indicates that the high melting region disappears with straining. In Fig. 7 a transmission electron microscopic (TEM) photograph of a highly deformed film (deformation temperature, $T = 115°$ C, $\epsilon = 100\%$) is shown; no change in the structure of the material can be detected.

4. Discussion

Every proposed model for high modulus polyethylene prepared by the method described above

TABLE I Young's modulus values of samples deformed at different temperatures

Set number	Deformation (%)	Temperature of deformation (° C)	Young's modulus (GPa)
I	0	–	20
	30	95	19.2
	65	95	16.1
	75	95	12.4
II	67	80	9.2
	67	95	7.7
	67	115	6

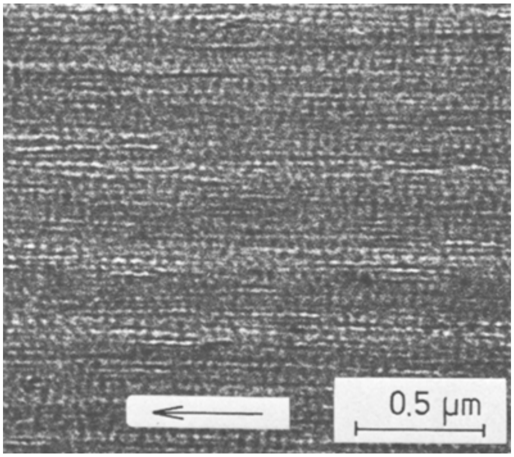

Figure 7 Phase contrast electron micrograph of a polyethylene film deformed about 100% at 115° C. Note the lamellar separation but the presence of the images of the needle-like crystals.

should explain satisfactorily the following experimentally observed facts:

(1) The disappearance of the higher melting peak in DSC scans (Fig. 3).

(2) The drop in Young's modulus after high deformation (Table I).

(3) Strong strain hardening at low deformation (Fig. 5).

(4) Strain softening at higher values of deformation (Fig. 6).

Numerous models [3, 6, 15] based on morphology have been suggested to explain mechanical properties. The first one deals with an interlocking of lamellae [3], the second one is a fibre-composite model [6] considering the shish as a stiff component and lamellae as the soft phase of the matrix and the third one is a crystalline network model [15] where the needle-like crystals act as physical tie points in the structure. The model based on the interlocking of the lamellae considers only the lamellar part on deformation. This is in contrast to our first observation (disappearance of high melting part) mentioned above and, hence, cannot be applied to our material.

The structure of polymeric materials in terms of fibre-composite and crystal network models can be considered either as composite materials or as cross-linked reinforced materials. The results of the present study will be discussed from the point of view of the fibre-composite model since the structure in our films has a great resemblance to fibre reinforced materials. The following mechanisms may explain the disappearance of the higher melting point (Fig. 3), the drop in Young's modulus after deformation (Table I) and the strain softening effect (Fig. 6).

(a) The reinforcing needle-like crystals fracture during deformation.

(b) The adhesion between the needle-like crystals and the matrix is weakened during deformation, i.e., modification of the interface.

Both mechanisms are schematically illustrated in Fig. 8. For simplicity, the soft lamellar matrix is eliminated in this figure. The disappearance of the higher melting point may arise either from the shortening of the needle-like crystals (melting point depression) or from the lesser constraint exerted by the matrix molecules at the interface as the molecules from the needle-like crystal matrix interface are peeled off (melting point

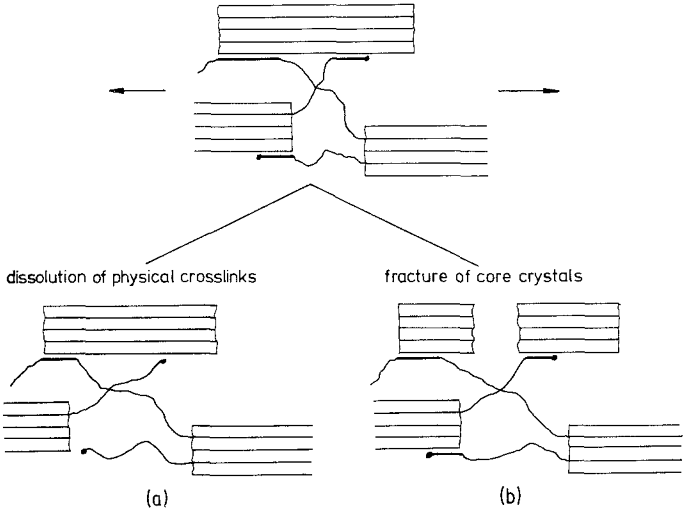

Figure 8 Schematic illustration of two possible mechanisms after the deformation: (a) ·Peeling off the molecules from the surface of needle-like crystals, i.e. loosening of the interface and (b) breaking of needles.

decrease due to increase in the entropy of matrix molecules) on deformation.

The drop in Young's modulus may either result from the smaller aspect ratio [16] after fracturing the needle-like crystals or from the lower adhesive forces between the needle-like crystals and the matrix. The same arguments can be applied to the strain softening behaviour observed after higher deformations.

From TEM observations (Fig. 7) no definite conclusion can be drawn for both models as the resolution is not sufficient to image very small fracture faces in the needle-like crystals. However, from the electron micrographs of drawn samples it appears that the image of the needle-like crystals is continuous and that they are not fractured on deforming the films. The major point favouring the adhesional weakening model is the drop in the Young's moduli with increasing deformation temperatures (Table I). For the same amount of straining of the samples it is difficult to understand an easier mechanism of fracturing of the needle-like crystals at higher deformation temperatures. It is more likely that the molecules are repelled or isolated at the interface at higher temperatures rather than at lower deformation temperatures.

In the crystalline network model, the behaviour of the material during straining may be similar to that described by the Mullin's effect [17] in particle reinforced plastics. The strong strain hardening observed at lower deformations as well as lower temperatures may be due to the straining of molecules which connect the needle-like crystals. Further experiments are in progress to investigate the effect of work hardening, with the help of deformation calorimetry, on different materials having needle-like crystals and only amorphous matrix composition (e.g., polybutene-1-polytransisoprene).

5. Conclusion

Straining of polyethylene films having a shish kebab morphology in the temperature range 80 to 115° C results in strain softening of the material and in a decrease of Young's modulus. These observations are in contrast to all the results observed so far in stretching thermoplastic materials having a lamellar morphology. The reason for the different mechanical behaviour of both types of morphologies is attributed to the change of the interface between the shish crystals (needles) and the surrounding matrix material.

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