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Micellar morphology and its plastic deformation behaviour in ultra-high molecular weight polyethylene

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Highly oriented samples from ultra-high molecular weight and normal high-density polyethylene (UHMWPE, HDPE) were prepared under the same experimental conditions. The morphology of the UHMWPE, investigated by transmission electron microscopy, was found to be oriented micellar, while the HDPE samples had a shishkebab morphology. Tensile test experiments under cyclic loading conditions exhibit a strain-hardening effect (increase in stress for the onset of plastic deformation) for HDPE, while the UHMWPE shows a decrease in Young's modulus, which is attributed to similar molecular mechanisms as for the Mullins effect in particle-filled elastomers.

1. Introduction

The stress–strain behaviour of polymers is strongly connected to morphologies. Typical shapes of those curves are obtained in spherulitic, stacked lamellar or needle-crystal morphologies [1–3], respectively. Yet, little is known about the details of the micellar morphologies themselves or about their stress–strain correlations. Because block copolymers find increasing applications as thermoplastic elastomers, and their morphologies have been identified to be micellar in certain composition ranges [4], more interest has been directed towards their morphology/mechanical properties relationships [5, 6]. On the other hand, oriented micellar morphologies can also be found in thermoplastic semicrystalline homopolymers, when they are crystallized under high strain rates and high undercooling [3]. Crystallites of about $10 \times 10 \times 10\,\mathrm{nm}^3$ form the micellar units, which are strongly interconnected by a large number of strained tie molecules. This morphology can also be characterized by a needle-crystalline morphology, in which the aspect ratio of the needle-crystals, l/d (l = length of the needle crystals, d = diameter) is about one, and the crystals are embedded into an oriented amorphous matrix. High molecular weight material favours the formation of this morphology, because the nucleation density under extensional flow conditions is high but the crystal growth rate is low, due to the high entanglement density of the molecules compared to lower molecular weight material. Under similar processing conditions, in lower molecular weight materials, stacked lamellar or needle-crystal morphologies may develop (depending on strain rate), while in the higher molecular weight polymer, the oriented micellar morphology is formed over a wide range of processing conditions.

It was the purpose of this work, to investigate the morphologies of ultra-high molecular weight polyethylene (UHMWPE) and medium range molecular weight PE, crystallized under similar strain and temperature conditions, and to compare their mechanical properties obtained in tensile test experiments.

2. Experimental procedure

The polyethylene used was Lupolen 6021D with a melt flow index (MFI 180/2.16) of 0.2 g/10 min from BASF company and UHMWPE from Polialden Petroquimica S.A. (Brazil) with $M_W = 3.5 \times 10^6\,\mathrm{g\,mol^{-1}}$. Highly oriented samples were prepared according to the method of Petermann and Gohil [7]: a 0.3% solution of the polymers in decalin was poured on a glass plate, which was heated to 130 °C. After the solvent was evaporated, the thin polymer film ($\approx 1\,\mu\mathrm{m}$) was picked up on a motor-driven cylinder which allowed about 200 layers to be wound up. The velocity of the cylinder (pick-up rate) was $4\,\mathrm{cm\,s^{-1}}$. Single layers were directly (without additional preparation) used for the investigations in the transmission electron microscope (TEM). The TEM used was a Philips 400 T operated at 100 kV. For tensile tests, 200 layers were laminated on the cylinder. The laminates were pressed in a hot press at 115 °C. Pressure and time were adjusted such that during

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pressing, no measurable flow of the laminates occurred and that the samples appeared optically transparent after the treatment. The pressed laminates were cut into ribbons of 65 mm × 4 mm with their long direction parallel to the draw direction of the film. The tensile tests were performed in a Zwick 1445 tensile testing machine with a deformation rate, $\mathring{\varepsilon}$, of 12.5% min^{-1}. For the thermal tests, a Heraeus DSC 500 differential scanning calorimeter with a heating rate of $10\,^{\circ}\text{C min}^{-1}$ was used.

3. Results and discussion

3.1. Crystal morphology

Alignment of the chain axis parallel to the drawing direction is the most important result when thin, electron-transparent films are prepared according to the Gohil and Petermann method [7]. The molecular alignment, however, can lead to different crystal morphologies which mainly depend upon the drawing ratio. Usually, optimum film drawing conditions with a maximum natural drawing ratio are observed at temperatures which are just above the highest crystallization temperature of the relaxed undercooled melt. Although a similar optimum drawing temperature of about 130 °C was found for both polyethylene materials, a much better drawing performance was noted for normal HDPE with an approximate drawing ratio of $\lambda \geqslant 5$ against $\lambda \leqslant 3$ for the UHMWPE material. This difference in drawing ratio led to a significant change in crystal morphology, as shown by electron microscopy observations and DSC measurements.

As indicated by a comparatively stronger phase contrast under bright-field conditions, drawn HDPE films appeared to be characterized by a higher crystallinity and a better fibre structure as judged from its continuous areas of stacked lamellar and an apparently higher shish content, Fig. 1. A higher degree of preferred orientation and therefore of crystalline chain-axis alignment in the case of the lower molecular weight material can also be observed from electron diffraction patterns which show the molecular axis to lie horizontally in Fig. 1. An increase in crystallinity and a higher degree of preferred orientation would both be consistent with the higher drawing ratios for HDPE during thin-film preparation.

Dark-field observations were employed in order to confirm the different crystal morphologies of normal HDPE and UHMWPE material. In Fig. 2, the higher shish content of HDPE can be recognized from a better alignment and a higher average aspect ratio when using $hk0$ as the operating reflection. Lamellar contrast on dark-field images formed by equatorial reflections frequently appears "patchy", due to bending of the lamellae in thin films around the molecular axis. A more continuous contrast for single lamellae can then be observed on dark-field images

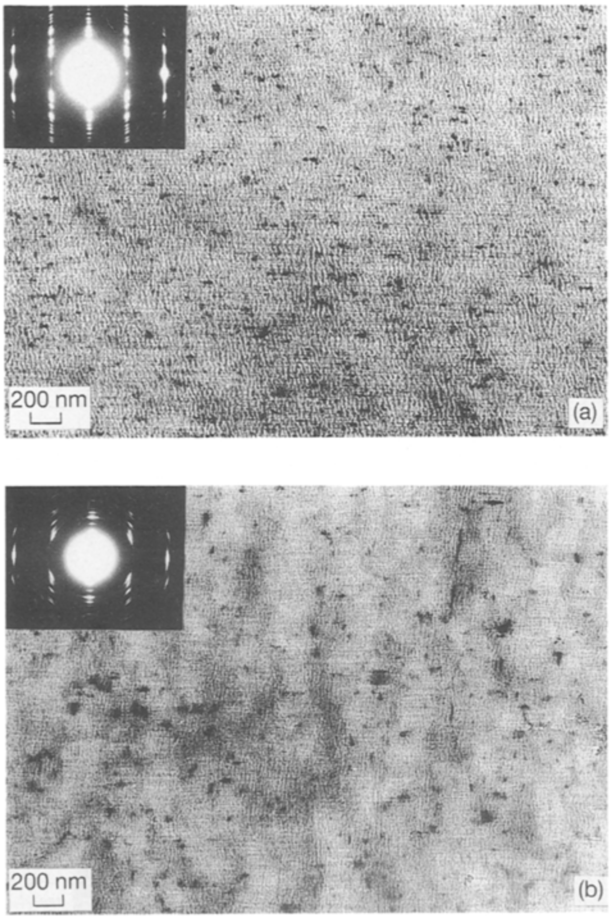

Figure 1 Bright-field transmission electron micrographs of a single layer of (a) HDPE and (b) UHMWPE. The electron diffraction patterns are inserted. Molecular directions are horizontal.

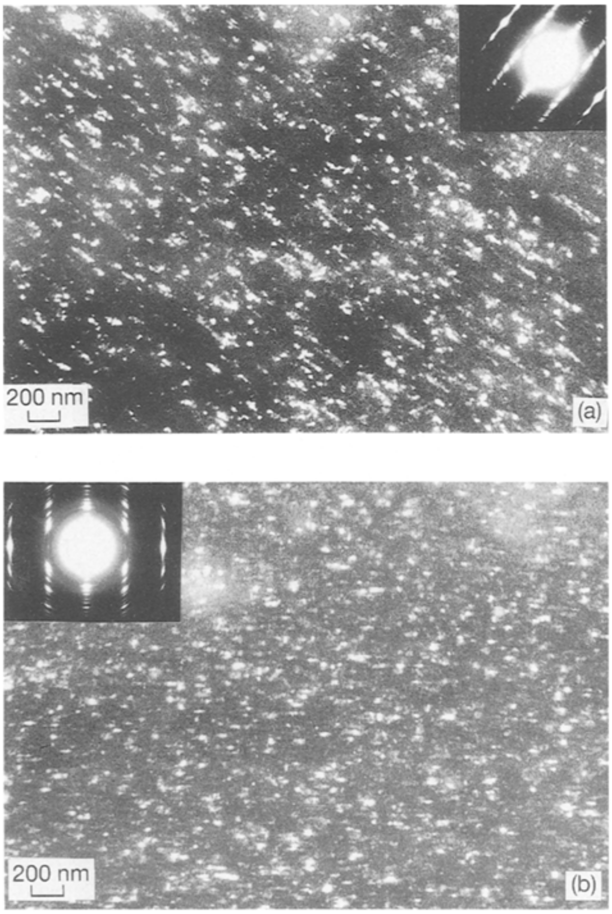

Figure 2 Dark-field transmission electron micrographs ($hk0$ operating reflections) of a single layer of (a) HDPE and (b) UHMWPE. The molecular directions can be seen from the inserted diffraction patterns.

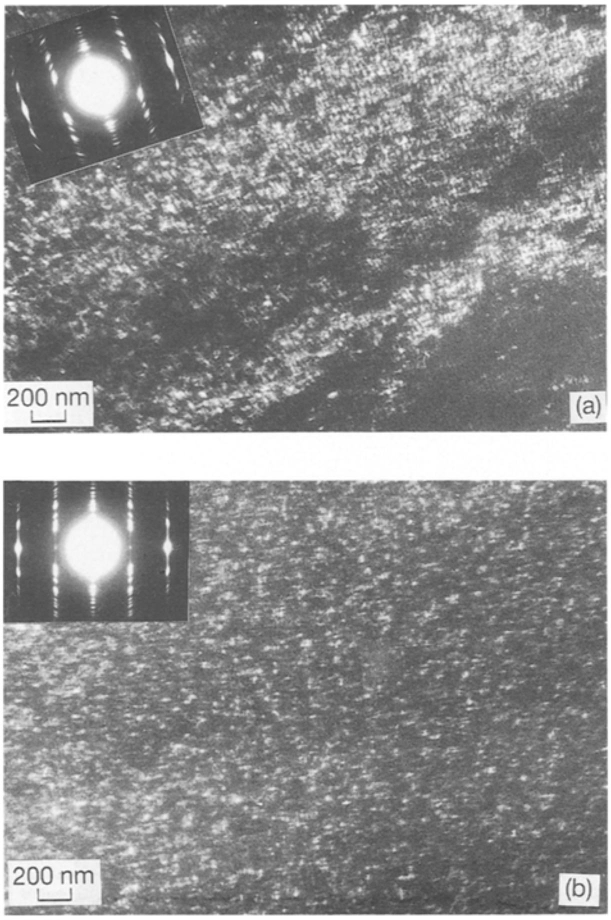

Figure 3 Dark-field transmission electron micrographs (00*l* operating reflections) of a single layer of (a) HDPE and (b) UHMWPE. The molecular direction can be seen from the inserted diffraction patterns.

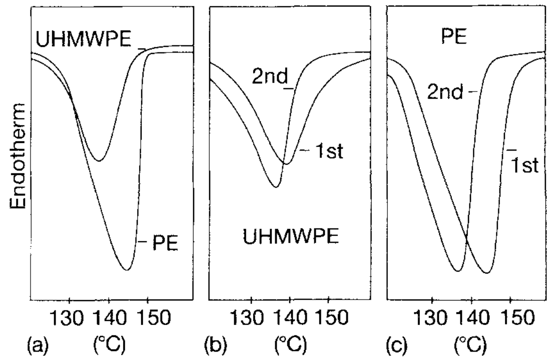

Figure 4 DSC traces of (a) the as-prepared samples, and the first and second heating traces of (b) UHMWPE and (c) HDPE.

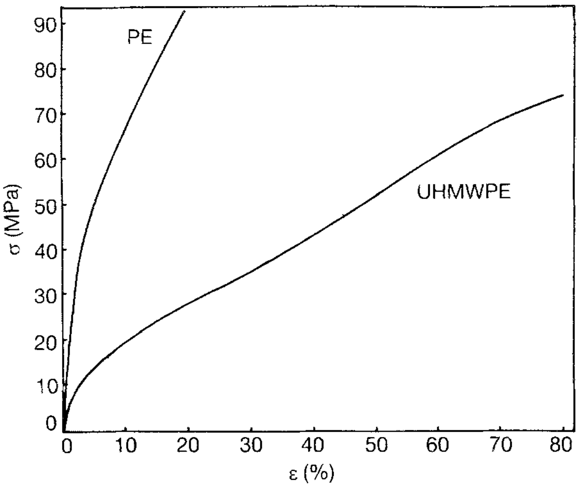

Figure 5 Stress–strain curves to fracture of HDPE and UHMWPE.

formed by the 002 reflection. Such dark-field images in Fig. 3 confirm the presence of stacked lamellae in parallel fibre orientation for the HDPE material, while the crystalline regions of the UHMWPE material continue to show a "patchy" distribution. From all such evidence, a normal shish-kebab morphology can be assigned to the drawn HDPE samples, while UHMWPE films can best be described by an oriented fringed-micelle morphology.

The electron microscopy observations of single thin-film layers were corroborated by the results of DSC measurements conducted on multilayered material which was prepared for mechanical testing, Fig. 4. Melting peaks of the two materials, obtained under identical conditions (heating rate, weight), confirmed the higher crystallinity in the case of HDPE, Fig. 4a. In addition, the HDPE shift in peak temperature can be explained by a higher proportion of shish crystals, which are known to superheat, due to a lower configurational melting entropy. Such interpretation was confirmed by a second DSC run which exhibited a decrease of the melting peak temperature, due to the absence of extended-chain crystals, Fig. 4b and c.

3.2. Plastic deformation behaviour

It is well known that the mechanical properties of semicrystalline polymers depend strongly upon their crystal morphology. As expected, a higher stiffness and also a lower ductility was shown by the well-developed shish-kebab structure of HDPE during tensile testing, Fig. 5. Such behaviour can easily be explained by higher crystallinity, a more perfectly aligned molecular orientation and a higher proportion of chain-extended shish crystals whose larger aspect-ratio has been shown to increase the strengthening effect which the amorphous matrix experiences due to the presence of harder, second-phase crystalline particles [8].

UHMWPE samples, on the other hand, presented tensile curves, Fig. 5, the shape of which has similarity to the deformation behaviour of elastomers (rubber elasticity). The characteristic shape of such curves can, in this case, be derived from random-chain statistics and the deformation of a network. In order to extend the same deformation model to the morphology of drawn UHMWPE samples, micellar crystals could be assumed to form the network junctions. Tensile tests under cyclic conditions (repeated cycles of loading and unloading) were performed to investigate further the deformation behaviour of the micellar morphology.

During cyclic testing, filled elastomers have shown the Mullins effect which describes a characteristic work-softening behaviour after each cycle of loading and unloading [9]. A very similar behaviour has been

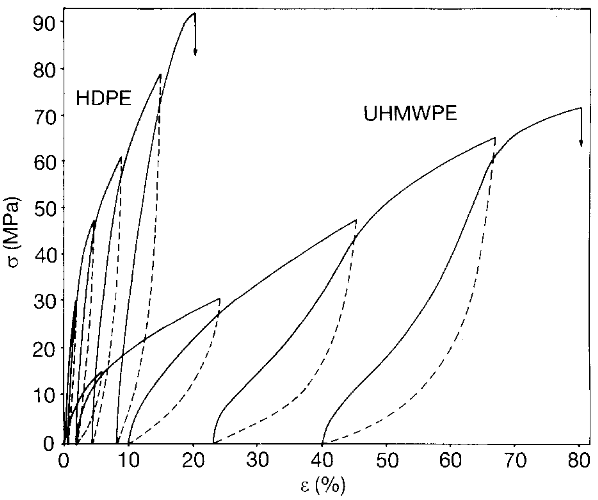

Figure 6 Deformation behaviour of HDPE and UHMWPE under cyclic loading conditions.

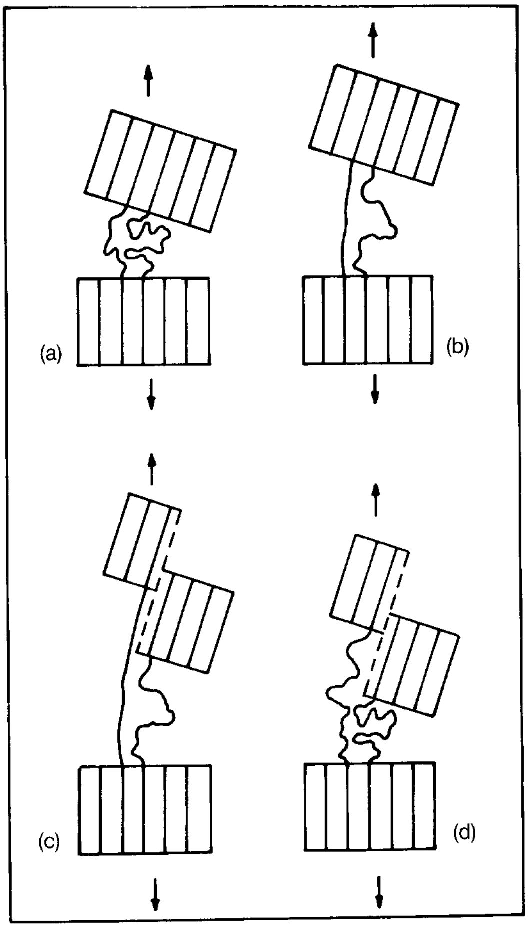

Figure 7 Structural model of the deformation of the micellar morphology: (a) unstrained, (b) strained to the extension of one tie molecule, (c) plastic deformation of the micellar crystal, (d) unloading. Note that the length of the left tie molecule has increased.

reported to occur in thermoplastic elastomers [5]. The basic structural concept, which has been used to explain the Mullins effect, is that fully extended chain segments are pulled loose from the filler particles during a previous loading cycle. As a result, the smaller number of load-bearing, extended-chain segments will lead to the formation of "stress valleys" upon subsequent reloading. As shown in Fig. 6, precisely such a behaviour can be recognized for UHMWPE samples during the later stages of deformation. In Fig. 7, a model is presented which would explain the observation of a Mullins effect by plastic deformation of the crystalline phase. As an example of plastic deformation, shearing of the micellar crystal is supposed to free a formerly extended amorphous chain segment from its crystalline junction. During reloading, the average length of the amorphous chain segments between the network's link positions will have increased, thus leading to lower stresses of an equivalent level of strain. On the other hand, the cyclic stress–strain behaviour of the HDPE exhibits a strain hardening with increasing numbers of cycles (Fig. 6). The increase of flow stress (onset of plastic deformation) has been observed previously in polybutene-1 and polyethyleneterephthalate (PET) samples containing shish morphologies [3] and was attributed to displacements of the shish crystals during straining. The same arguments hold for the explanation of the stress–strain curves of the HDPE.

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