Scanning electron microscopy of oriented high density polyethylene

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With 9 figures

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1. Introduction

Previous work using small-angle X-ray scattering (SAXS) measurements and surface replica transmission electron microscopy (TEM) has shown that cold-drawn high density polyethylene (HDPE) has a microfibrillar structure (e.g., 1, 2). Bonart and Hosemann (1) deduced from SAXS patterns that some of the microfibrils occur singly while others aggregate into microfibrillar bundles (or fibrils). A microfibril consists of rather imperfect crystalline and amorphous blocks arranged in series along the length of the microfibril. According to Peterlin’s molecular model for polyethylene fibre (2), microfibrils are connected by tie molecules and aggregate into fibrils, which themselves are connected by interfibrillar tie molecules. On being annealed with free ends, cold-drawn HDPE shrinks and a lamellar morphology of well-developed crystalline and amorphous regions arises (e.g., 3–8).

The purpose of this work is to use the technique of scanning electron microscopy (SEM) to observe these structures directly in cold-drawn and cold-drawn/annealed HDPE. In the light of the present investigations a model for the cold-drawing mechanism in HDPE sheet is proposed, which also explains the occurrence of the 4-point SAXS pattern found for annealed material.

2. Experimental section

The material used for the investigations was “Rigidex 9” HDPE (B. P. Chemicals Ltd.). Sheets 2 mm thick were compression-moulded at 160 °C and quenched into iced water. Subsequently they were cut into strips 60 mm wide and, with initially only 10 mm between the grips of the testing machine, drawn at room temperature (20 °C) at a rate of 10 mm/minute. The sheets necked and became opaque. A drop in density from 0.966 to 0.923 g/cm³ due to drawing indicated the formation of voids.

For the investigations, specimens were cut out of the central region of one of the drawn sheets where the draw ratio (λz) was 11.5, the thickness contraction ratio (final thickness/initial thickness) λX was 0.18 and the width contraction ratio λY was 0.50.

Samples were annealed for 1 hour with free ends by being immersed in silicone oil which had been previously heated to the required temperature. All samples were subsequently cooled in air.

Fracture surfaces of the specimen interior were produced by freezing strips under liquid nitrogen and correspondingly splitting them so as to expose YZ and XZ sections. Figure 1 gives a definition of the directions in the specimen sheet.

After fracture surfaces had been produced, annealed samples were lightly etched in fuming nitric acid of density 1.50 g/cm³ at 70–80 °C for times between 15 and 60 minutes. The etchant attacks and removes preferentially the noncrystalline material (9).
Specimens were subsequently coated with a 10 to 20 nm thick gold film by means of a "cool" sputter coater (Polaron Ltd., Model E5100). The advantage of this equipment over conventional sputter coaters is that electrons which would otherwise cause specimen heating are deflected from the sensitive surface by means of a suitable magnet. In addition, the specimen table is cooled to about 5 °C by a Peltier element.

Investigations were carried out using a Philips PSEM 500 scanning electron microscope. The majority of observations were made using an operating voltage of 25 kV, an objective aperture of 200 μm and a probe diameter of 6 nm at magnifications over 10,000 times. Images were obtained using the secondary electron signal. To obtain the best brightness and topographical contrast conditions, specimens were usually tilted at 45 ° to the beam.

Auxiliary information on the crystallographic orientation was obtained by means of wide-angle X-ray scattering (WAXS), and on the morphology using a small-angle X-ray camera with pinhole collimation. In addition, the shrinkage behaviour of cold-drawn HDPE heated at 1 °C/minute was measured using a creep apparatus described elsewhere (10).

3. Results and discussion

3.1 Cold-drawn HDPE

3.1.1 The microfibrillar structure

SEM micrographs of cold-drawn HDPE (fig. 2) showed a structure attributable to microfibrils oriented along the draw direction, thus confirming previous work. The microfibrils appeared to be at least several microns long, and had a smallest observable diameter of approximately 35 nm. No periodicity along the microfibrils was detected in the SEM for cold-drawn HDPE. This is not surprising, since the SAXS meridional intensity is very diffuse, indicating that the distinction between the crystalline and non-crystalline regions along the microfibrils is not pronounced. In addition, the SEM method involves essentially a view of the topography of the microfibrillar surface.

In general, it was found that XZ fracture surfaces were much “rougher” than YZ fracture surfaces. The reason for this lies in the particular way in which the sheet drew, and will now be discussed in the next two sections.

3.1.2 Drawing mechanism

Firstly, WAXS and SAXS measurements showed that the cold-drawn sheet appeared to be transversely isotropic both from a crystallographic and from a morphological point-of-view respectively, as is normally found for uniaxially drawn material. However, the macroscopic sheet deformation was anisotropic in a plane at right angles to the draw direction (i.e. $\lambda_\alpha \neq \lambda_\beta$).

In our case, relative thickness changes exceeded relative width changes by a factor of approximately 3:1. This effect is well-known for the drawing of sheet material. For example, Bonart (11) has considered the behaviour of poly(ethylene terephthalate) and nylon 6, while Seto and Hara (4), Ohde (8), Owen (12) and Buckley, Gray and McCrum (13) have described the behaviour of polyethylene.

In the present case, the specimen grips exerted lateral constraints (in the Y direction), such that the drawing neck was most pronounced in the

Fig. 2. Cold-drawn HDPE (a) XZ surface (b) YZ surface.