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Observations of Shish-Kebabs in Solvent-Treated Fracture Surfaces of Polyethylene

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SUMMARY

Shish-kebabs are observed by scanning electron microscopy on fracture surfaces of a low molecular weight, high-density polyethylene treated by hot p-xylene. The shish-kebabs observed originate from the fibrils of the fracture surface. It is suggested that the larger fibrils are partially dissolved and that the partially dissolved molecules recrystallize on cooling forming the lamellar-like structures of the shish-kebabs. The less developed fibrils of the fracture surface dissolve completely.

INTRODUCTION

In several papers (MEHTA and WUNDERLICH 1974, DLUGOSZ et al 1976, WINRAM et al 1978, GEDDE and JANSSON 1982a), the possibility of selectively dissolving polymer crystals of low thermal stability and leaving unaffected crystals of higher melting point has been demonstrated. In these papers, polyethylene (PE) has been studied and p-xylene has been used as the solvent. For a linear PE sample it has been shown that the dissolution temperature of a crystal in p-xylene is about 30 K lower than its melting point (GEDDE and JANSSON 1982a). For linear polyethylenes, this seems to apply to all the crystals, thin as well as thick, of the polycrystalline samples (GEDDE and JANSSON 1982a).

In an experimental programme on polymer morphology-fracture properties relationships, fracture surfaces of isothermally crystallized PE samples were treated with hot p-xylene. The temperature of the solvent was chosen so that only the so called segregated component was dissolved and removed from the samples. The segregated component is the material not able to crystallize at the isothermal temperature. Instead, this material (mainly low molecular weight species) requires a higher degree of supercooling to crystallize. This technique allowed us to observe how fracture path relates to morphology. A typical micrograph of this kind is shown in Fig.1. A further paper deals with this subject (GEDDE, EKLUND and JANSSON 1982b).

However, in some of the solvent-treated fracture surfaces some quite different structures were observed. These structures which are not very different from the shish-kebabs reported by PENNINGS and KIEL (1965), are the subject of this paper.

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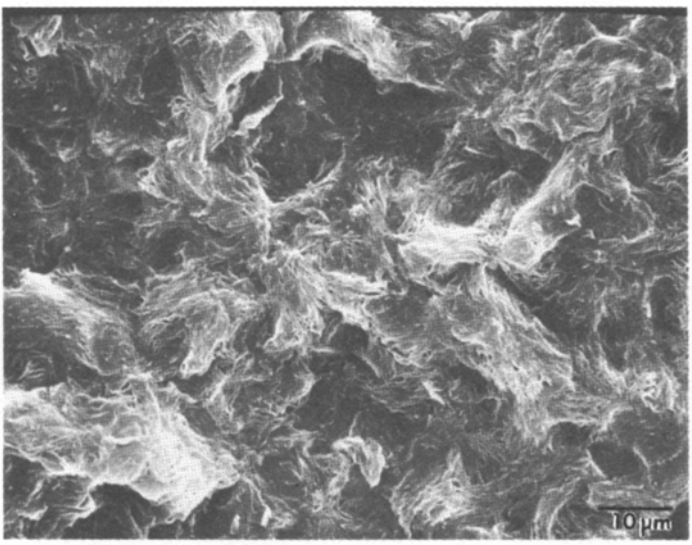

Figure 1. Scanning electron micrograph of solvent-treated fracture surface from the region of slow crack growth. The sample was subjected to an uniaxial tensile stress of 9.94 MPa at 60°C and failed after 0.35 h

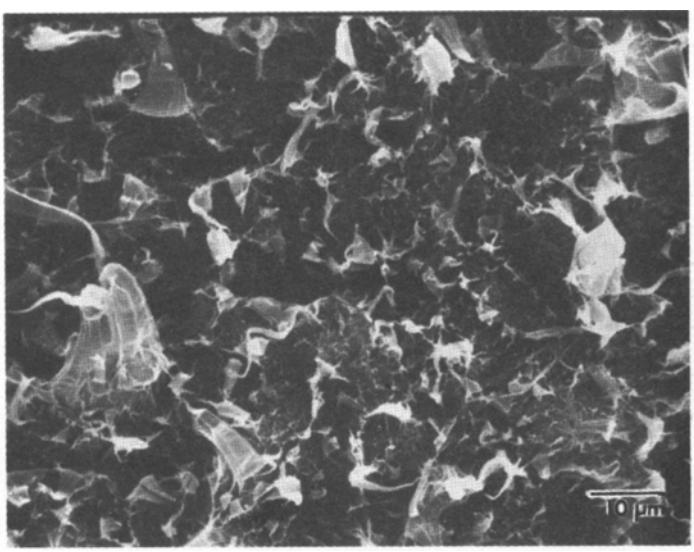

Figure 2. Scanning electron micrograph from the region of slow crack growth. The sample was subjected to an uniaxial tensile stress of 9.94 MPa at 60°C and failed after 0.35 h

EXPERIMENTAL DETAILS

Dumb-bell shaped specimens were prepared from a high-density polyethylene ($\bar{M}_n$ = 8400 and $\bar{M}_w$ = 90000). The samples from the melt isothermally crystallized at 125°C for 24 hours and then rapidly cooled to 25°C were fractured by the action of constant uniaxial tensile loads at 60°C. The fractures were brittle on a macroscopic scale. However, with the aid of the scanning electron microscope, ruptured fibrils could be observed on all the fracture surfaces (Fig. 2).

Samples containing the fracture surface were cut from the specimens, treated by p-xylene at 102°C for 48 hours, washed in fresh solvent at 102°C, dried in vacuum for 150 hours, guld-sputtered and examined in a scanning electron microscope (SEM), an ISI Mini SEM. The temperature of the solvent was chosen so that a maximum of the segregated component was dissolved leaving the non-segregated component unaffected. This was verified by differential scanning calorimetry (DSC).

RESULTS AND DISCUSSION

Micrographs of the solvent-treated fracture surfaces showing the shish-kebabs are presented in Fig. 3.

From a comparison of Figs. 2 and 3a it is obvious that the shish-kebabs observed originate from the mechanically generated fibrils. The shape and size (length 10 to 30 μm and diameter 1 to 5 μm) of the larger fibrils is in agreement with the size of the shish-kebabs. Another feature is that the smaller fibrils present in Fig. 2 are not present as shish-kebabs in Fig. 3a. They must be less stable towards the solvent than the larger fibrils and are consequently dissolved.

The restructuring of the fibril into a shish-kebab must involve a dissolution of at least a part of the material of the fibril. However, the preservation of shape and size indicates that the dissolution of the material of the fibrils is not complete. The micrographs of Figs. 3 b and c show that the distance between adjacent lamellae of the shish-kebab is of the order of 0.5 μm. This fact excludes the possibility that the shish-kebabs are produced by the dissolution and removal of parts of the material of the fibrils. Instead, it suggests that the lamellae of the shish-kebabs are formed by the crystallization of partially dissolved molecules of the fibril. This occurs during the subsequent cooling (drying) of the solvent-treated sample. That entirely dissolved molecules would crystallize on the remaining undissolved fibril is unlikely since the samples were washed with fresh (hot) solvent after treatment. The thickness of the lamellae of the shish-kebabs as measured from the micrographs is of the order of 1000 Å. However, the gold-sputtering thickens all formations on the surface including the lamellae. Based on an equation relating the thickness of the gold layer to the conditions of the sputtering (applied voltage, time of sputtering, etc), the thickness of the lamellae can be estimated to be of the order of hundreds of Ångströms. Another question of relevance is why certain parts of the fibril are more stable towards the solvent than others. It is known that the peripheral part of the

fibrils is of lower stability (melting point) than the central parts (PETERLIN 1979). Kinetic factors may also be influencial. By the technique used in the present study applied to isotropic linear PE we have shown that equilibrium dissolution is reached within 10 hours (GEDDE and JANSSON 1982a). However, the structure of the material within the fibrils is different and possibly less accessible to the solvent.

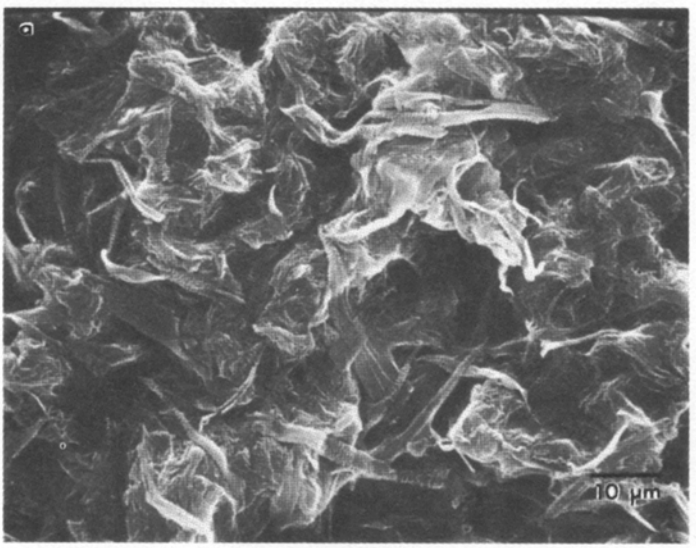

Fig. 3a

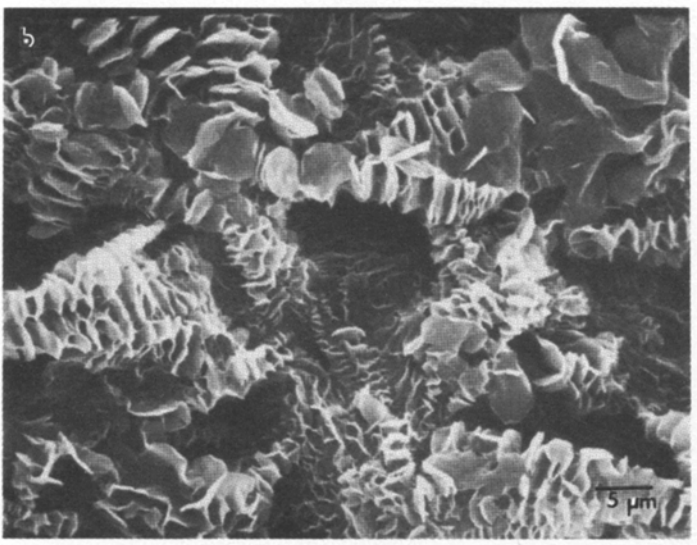

Fig. 3b

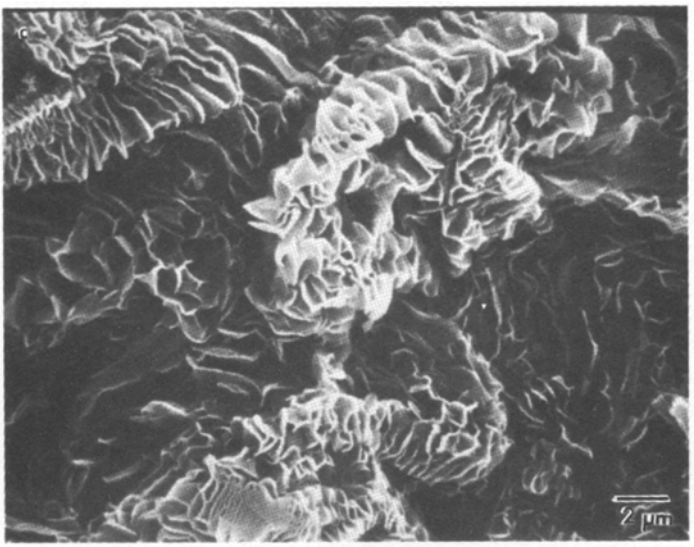

Fig. 3c

Figure 3. Scanning electron micrographs of solvent-treated fracture surfaces: (a) from a sample subjected to an uniaxial tensile stress of 9.94 MPa at 60°C; (b) from the same sample as in a, but at a higher magnification; (c) from a sample subjected to an uniaxial stress of 6.08 MPa at 60°C. Failure time = 67.9 h

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