Microscopic Observations Relating Fracture Morphology to Molecular Weight Segregation in Melt-Crystallized Polyethylene

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SUMMARY

Fractography by scanning electron microscopy (SEM) of samples of a low molecular weight, high-density polyethylene from the melt isothermally crystallized at 125°C, together with SEM on these samples treated with p-xylene (including fracture surfaces), polarized light microscopy, differential scanning calorimetry and gel permeation chromatography have provided evidence that fracture preferentially develops along a weakest link path defined by regions of segregated low molecular weight material. The segregated material is to a considerable extent accumulated in the spherulite boundaries.

INTRODUCTION

Molecular fractionation (molecular segregation) is a phenomenon which occurs during the solidification of crystalline polymers. The origin of this fractionation is the fact that all polymer systems have a multicomponent character and that the different molecules exhibit varying tendencies to crystallize. At each temperature of crystallization there exist in principle two types of material: 1) molecules that may crystallize at the particular temperature (in this paper this type is referred to as non-segregated), 2) molecules that are not crystallizable at this temperature (referred to as segregated component). Instead, these species require a higher degree of supercooling to crystallize. It has been shown by several authors, e.g. MEHTA and WUNDERLICH (1975), that fractionation occurs due to differences in molecular weight. Low molecular weight material has a smaller tendency to crystallize. Differences in degree of branching in polyethylene have also been shown to cause fractionation on crystallization (HAWKINS and SMITH 1958).

The lower stability (melting point) of the segregated component (compared with the non-segregated component) makes it possible to separate this material from the rest of the sample by solvent extraction. This has been demonstrated on melt-crystallized PE in several reports (MEHTA and WUNDERLICH 1975, DLUGOSZ et al 1976, WINRAM et al 1978, GEDDE and JANSSON 1982a). Microscopy has provided evidence that a large fraction of the segregated low molecular weight material is accumulated in the spherulite boundaries (WINRAM et al 1978, GEDDE and JANSSON 1982b), see Figs.1 and 3.
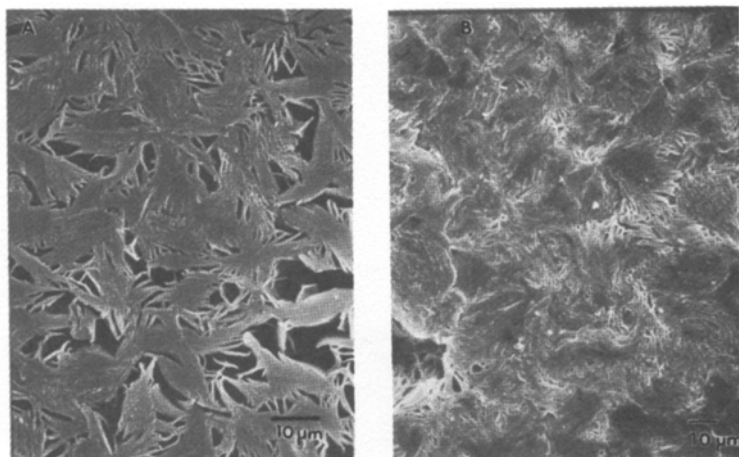
Figure 1. Scanning electron micrographs of solvent
(hot p-xylene)-treated polyethylenes. a) PE mate-
rial isothermally crystallized from the melt at $128^{\circ}C$
for 330 hours. b) The same PE isothermally
crystallized at $125^{\circ}C$ for 310 hours

In two reports (PHILLIPS and PATEL 1978, GEDDE et al 1981) fracture proper-
ties were investigated in relation to molecular weight segregation . The
data obtained indicated that samples which crystallized at a low degree of
supercooling were more brittle than those which crystallized during rapid
cooling. It was believed that the segregated low molecular weight material
formed a brittle phase through which fracture propagates more easily than
elsewhere. The aim of this paper is to present data from microscopic
studies which substantiate this idea.

EXPERIMENTAL DETAILS

Dumb-bell specimens of a high-density polyethylene were fractured by the
action of constant uniaxial tensile loads at 30, 45 and $60^{\circ}C$. All fractures
were brittle on a macroscopic scale. The material characteristics are as
follows: $\overline{M}_n$ = 8400, $\overline{M}_w$ = 90000 (by gel permeation chromatography), 6 methyl
groups/1000 carbons (by infrared spectroscopy). All the samples were iso-
thermally crystallized from the melt at $125^{\circ}C$ for 24 hours. This time was
long enough to ensure that fractionation was completed. This was verified
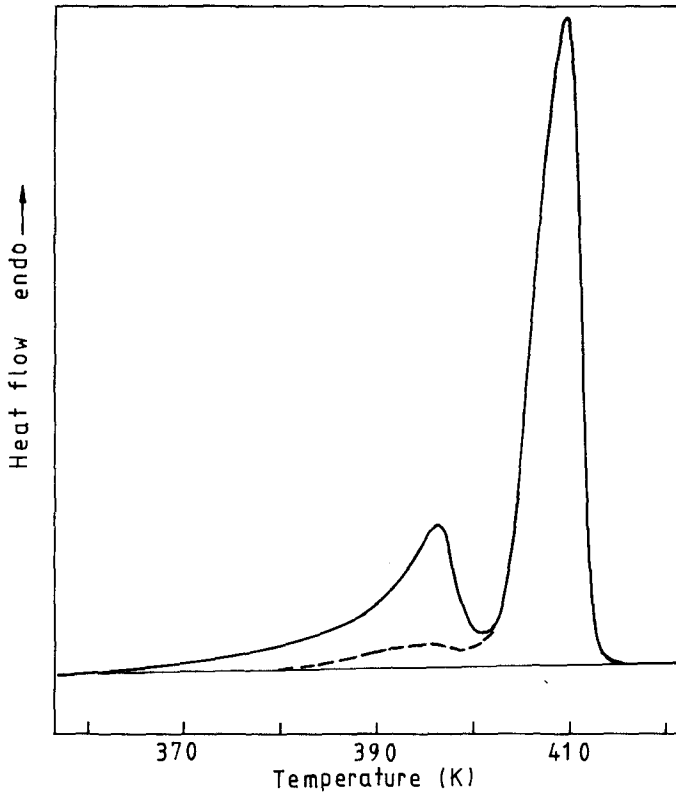by differential scanning calorimetry (DSC).

Figure 2. Melting endotherm of PE studied (solid line).
The fraction of segregated material (the area of the low
temperature peak/total area under the melting curve)
is 29 %. By solvent treatment (p-xylene of $102^{\circ}C$ for
48 hours) about 75 % of the segregated material is
selectively dissolved. The broken line shows the endo-
therm of the sample after solvent treatment

Figure 3. Polarized
light micrograph of
the PE material
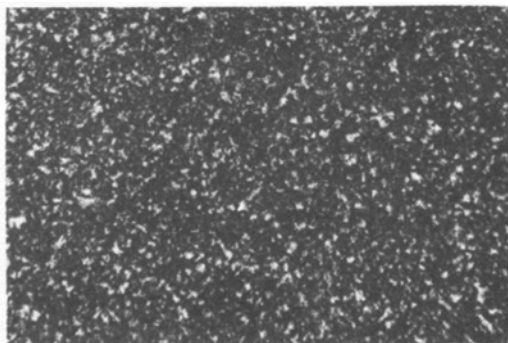
20 µm

Fig. 3 shows a polarized light micrograph of a 20 μm film of the PE studied. Note the similarity between the size of the spherulites of this micrograph and the size of the spherulite-like formations of Fig. 1.

The fracture surfaces obtained were examined in the scanning electron micro-scope (SEM), an ISI Mini SEM, after gold-sputtering.

Some fracture surfaces were also treated by p-xylene at $102^{\circ}C$ for 48 hours, washed in fresh solvent at the same temperature, dried in vacuum for 150 hours, guld-sputtered and examined in the scanning electron microscope. The temperature of the solvent was chosen so that a maximum of the segre-gated component was dissolved leaving the non-segregated component unaffec-ted. This was checked by DSC (Fig. 2).

RESULTS AND DISCUSSION

All the fractures considered in this paper are macroscopically brittle but, as can be seen in the scanning electron micrographs (Figs. 4c and d), the fracture surfaces are covered with fibrils having diameters ranging from 0.1 to 5 μm and lengths between 1 and 10 μm. It seems that the degree of plastic deformation is low at 25 and $40^{\circ}C$ (Fig. 4c), but higher at $60^{\circ}C$ (Fig. 4d).

The small fibrils were completely dissolved by solvent treatment. However, the larger fibrils dissolved only partially leaving shish-kebab structures as reported in another paper (GEDDE and JANSSON 1982c).

On all fracture surfaces, two zones can be observed (Fig. 4a): A circular or semi-circular zone of slow crack growth (stress intensity factor $< K_{IC}$) and a region outside this of rapid crack growth (stress intensity factor $> K_{IC}$). In only a few fracture surfaces is any difference observed in the fracture morphology in terms of degree of plastic deformation, see Fig. 4e.

Fig. 4b shows a rough surface characteristic for all fractures studied. Sharp edges with smoother areas in between are feature of the surfaces. It seems that the edges form the peripheral parts of sheaves, which are distributed in a stochastic manner all over the structure. The size of the sheaf formations is about 20 μm. This is also the size of the supermole-cular structures (spherulites or axialites) of this particular polyethylene, see Figs. 1a, b and 3. The boundaries of the spherulites (axialites) are composed of low molecular weight segregated material. The shape of the spherulites (axialites) is also similar to that of the sheaves of the fracture surface. The solvent-treated fracture surfaces showed this even more clearly, see Figs. 5a and b. The rapid crack growth regions of the fracture surfaces were also studied and the sheaf formations were observed as frequently as in the slow crack growth regions.
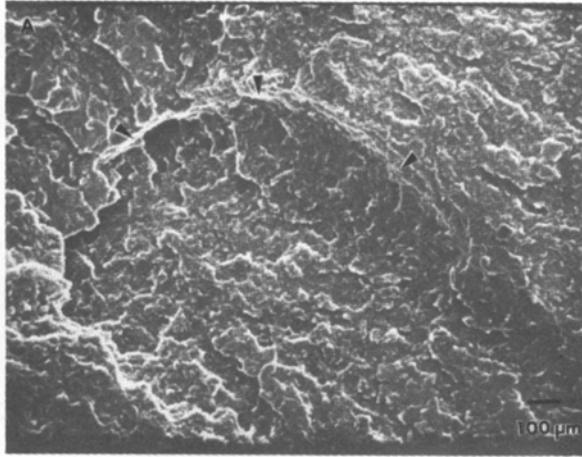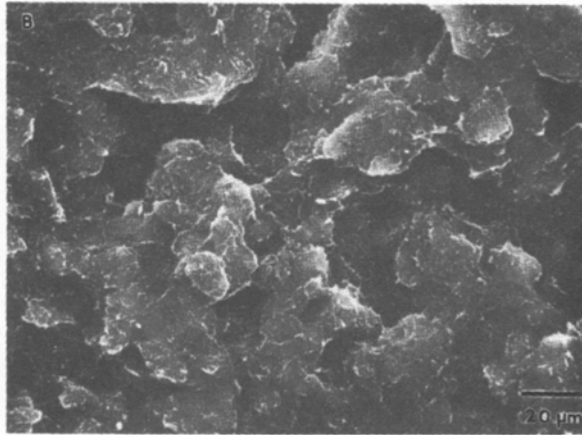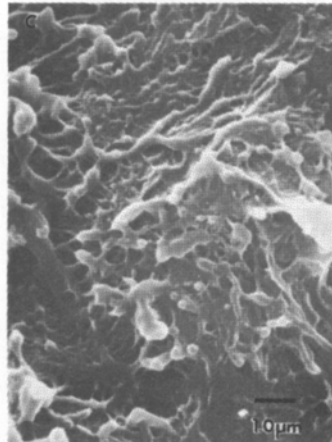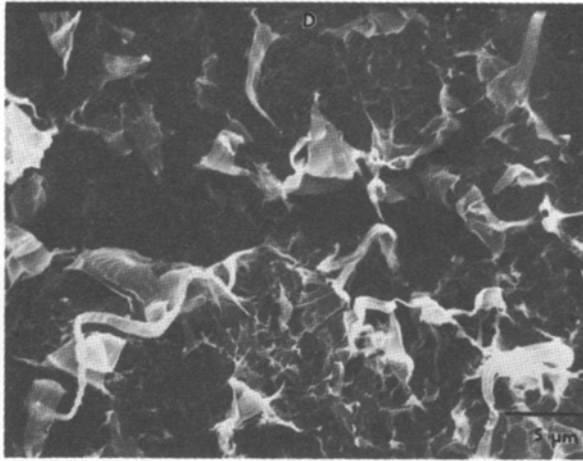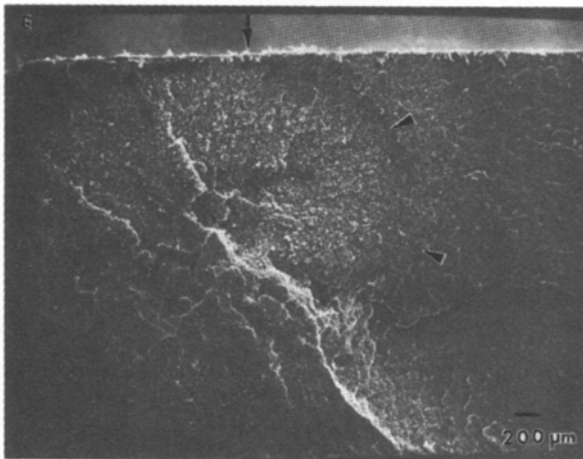
Fig. 4a

Fig. 4b

Fig. 4c

Fig. 4d

Fig. 4e

Figure 4. Scanning electron micrographs of fracture surfaces. (a) stress = 13.52 MPa, T = 45°C failure time = 0.27 h, note the circular region (slow crack growth). (b) stress = 13.52 MPa, T = 45°C, slow crack growth region. c) same as b), at a higher magnification, (d) stress = 9.9 MPa, T = 60°C, failure time = 0.35 h, slow crack growth region. e) stress = 9.9 MPa, T = 60°C, note the circular region (slow crack growth)
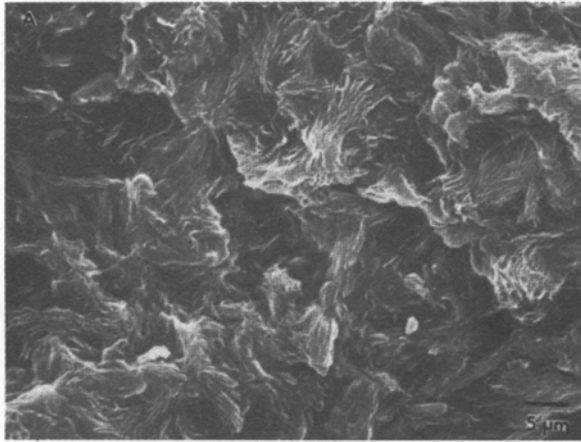
Fig. 5a.

Fig. 5b.

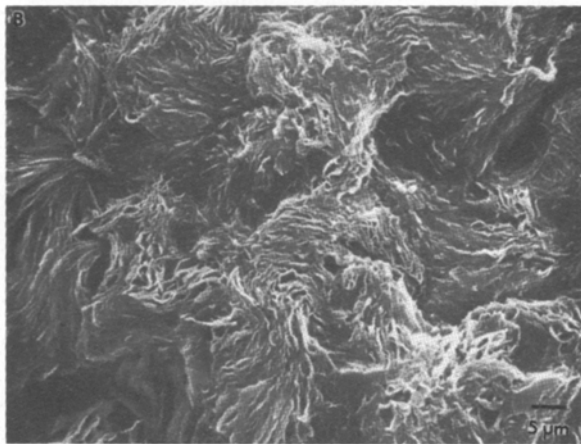Figure 5. Scanning electron micrographs of sol-
vent-treated fracture surfaces, both (a) and
(b): stress = 13.52 MPa, T = 45°C, failure time
= 0.27 h, slow crack growth region

Scanning electron microscopy of fracture surfaces (as obtained and after
treatment by hot p-xylene) provides indications for that fracture pro-
pagates preferentially according to a weakest link path defined by the seg
regated low molecular weight regions.The morphology of the latter (Fig.1)
shows a strong similarity to the boundaries of the supermolecular struc-
tures as observed by polarized light microscopy (Fig. 3). A more extensive
report on this is published elsewhere (GEDDE and JANSSON 1982 b). Evidence
that the segregated component is composed of low molecular weight material
has been obtained by GPC analysis and the average values for the segregated
component are as follows: $\bar{M}_n$ = 2900, $\bar{M}_w$ = 5400. For further details see
another report (GEDDE and JANSSON 1982a). The main reason why the segre-

gated low molecular weight component can be considered to be weak is that the concentration of interlamellar tie chains is low within this phase (for experimental evidence see e.g. VADIMSKY et al 1969) and under the action of stress only a few tie chains have to be broken to create (or propagate) a crack.

ACKNOWLEDGEMENTS

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