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Influence of molecular weight and branch content on the fracture behaviour of polyethylene

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The fracture behaviour of a range of polyethylenes with different molecular weights and side group content has been studied by means of a novel high-pressure tensile testing facility. The normally ductile specimens became brittle at high pressures, e.g. 700 MPa, so that the test results could be studied by means of linear elastic fracture mechanics. Oriented specimens were prepared by die-drawing to draw ratios of 5:1 and 9.5:1. The performance of the isotropic and oriented (longitudinal and transverse directions) materials were assessed using their K_{IC} values. Results were carefully compared in order to study the effects of molecular weight and low concentrations of small side groups on the fracture behaviour of polyethylene. The structure of the oriented polymers was characterised using wide-angle X-ray diffraction.

1. Introduction

In recent years, tough grades of polyethylene have been finding increasing utilization in gas and water pipe applications. Many polyethylenes are known to fail in a brittle manner under loads below their yield stress after a long period of time. However, limited fracture data are available for these increasingly important industrial polymers because they behave in a ductile manner under normal short-term conditions. Plane strain brittle failures for these tough polymers may be obtained only by using very thick specimens which make the test impractical. However, a novel test technique has been developed at Leeds University in which by carrying out a fracture test under high superimposed hydrostatic pressure it is ensured that failure occurs in a brittle fashion for polyethylenes which would fail in a ductile manner at atmospheric pressure [1–4]. This test technique is based on the fact that most polymers can be made to undergo a ductile to brittle transition when the yield stress, which increases with increasing pressure, exceeds the fracture stress [5, 6]. This is due to the fact that, at sufficiently high pressure, the plastic zone size of the polymers becomes so small that the fracture behaviour of the normally ductile polymers can be analysed by linear elastic fracture mechanics. This short-term high-pressure tensile test can thus enable the fracture toughness to be used as a quantitative quality control and also as a means to study factors affecting the fracture behaviour of these polymers. In the present investigation, different grades of polyethylene were carefully selected with a range of molecular weights and side group content. The performance of these polymers was enhanced by molecular orientation which was made possible by the new process of die-drawing [7]. The variation in mechanical properties was assessed using their K_{IC} values.

2. Materials

Seven different polyethylenes were used in the work. Their molecular characteristics, together with those for the homopolymer Hizex 7000F are shown in Table I (see Section 4.1). The homopolymers Unifos 2912

TABLE I Molecular characteristics for the polyethylenes used in this work

Grade	$\bar{M}_n$	$\bar{M}_w$	Branch type	Branch conc. (per 1000 C)
Hizex[a]	9 600	282 400	–	0
006-60[b]	16 900	109 100	–	0
Unifos[c]	23 900	174 000	–	0
002-55[b]	20 900	176 600	*n*-butyl	~ 1
H060-45[b]	27 000	232 900	*n*-butyl	~ 1.3
002-40[b]	20 500	182 600	*n*-butyl	~ 4
TR-418[d]	15 000	170 000	*n*-butyl	4.5
R40[b]	10 300	90 000	methyl	~ 5.6

[a] Mitsui Petrochemicals Ltd.
[b] B P Chemicals Ltd.
[c] Neste.
[d] Du Pont.

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and Rigidex 006-60, and the copolymers Rigidex 002-55, Rigidex H060-45, Rigidex 002-40, Rigidex R40 and TR-418 were also used.

3. Experimental procedure

3.1. Preparation of oriented sheets

All the oriented polyethylene specimens were prepared by a die-drawing technique developed at Leeds University [7]. The isotropic polyethylene billet for die-drawing was first prepared by melt extrusion. The polymer melt was fed from the extruder to the bottom of a vertical mould. A weight was placed on top of the polymer melt at the beginning of the process in order to reduce the formation of voids in the melt. The extruded polymer and the mould were then transferred and annealed in an oven in a vertical position at 180 °C for 10 h. The hot polymer was finally cooled to room temperature over a period of about 12 h. After cooling, the rectangular billet was machined to a suitable size and shape for drawing to the required draw ratio through a converging sheet-die of rectangular exit slot held at 100 °C.

3.2. High-pressure tensile testing

3.2.1. Preparation of specimens

Specimens were cut both from the undrawn isotropic billet and from the oriented sheet for the fracture testing. Two types of specimens were prepared from the oriented sheet: the longitudinal and the transverse specimens which were cut along, and perpendicular to, the draw direction, respectively. All specimens had a gauge length of 30.0 mm and a width of 15.0 mm. The thickness for the isotropic specimens was about 10.0 mm in order to ensure a brittle failure in the test. Symmetrical double-edge notches were cut first with a slitting saw, and then carefully sharpened with a notched razor blade which was attached to a hand-operated shaping machine to give a notch depth/half specimen width ratio, a/w, from 0.33–0.60 (Fig. 1).

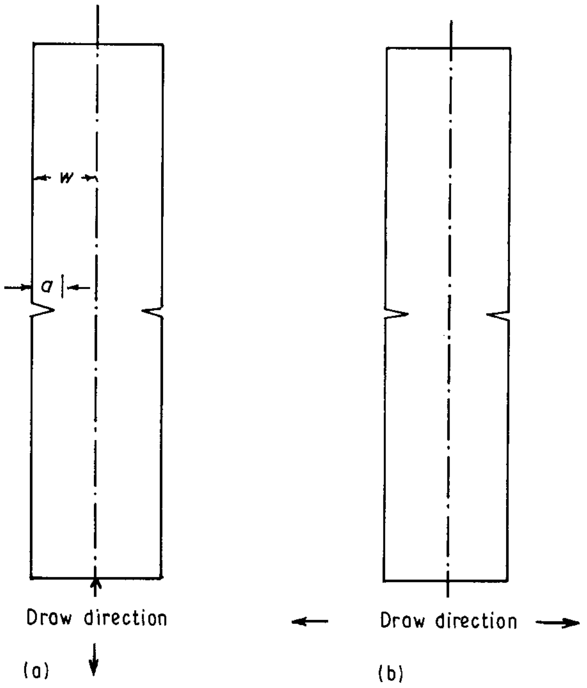

Figure 1 Double-edge notched specimens for high-pressure tensile tests. (a) Longitudinal specimen, (b) transverse specimen.

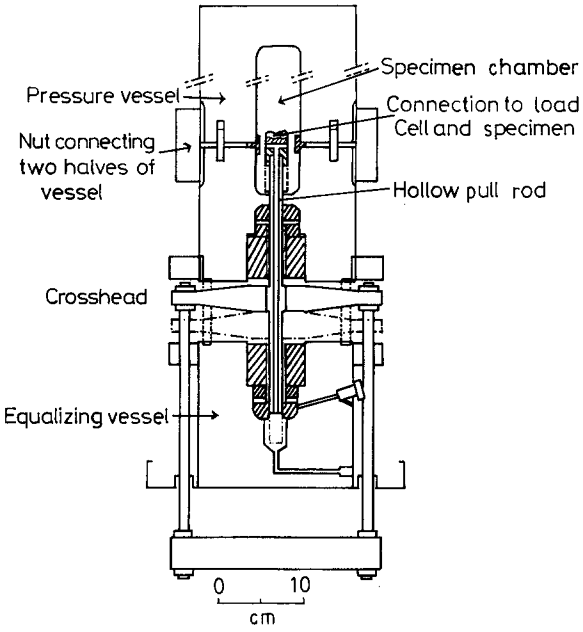

Figure 2 High-pressure tensile test apparatus.

3.2.2. Instrumentation

The high-pressure tensile testing machine (Fig. 2) was based on similar principles of design to that of a high-pressure torsional testing machine described by Rabinowitz *et al.* [6] and has been described by Sweeney *et al.* [8]. During the test, the specimen was gripped firmly by the jaws which were attached to the lantern and the hollow pull rod, as shown in Fig. 3. The specimen and the lantern were then placed inside the specimen chamber of the cylindrical steel pressure vessel (Fig. 2). High-pressure fluid was pumped into the testing machine to establish the required pressure at 700 MPa. This pressure was chosen because Sweeney *et al.* showed that when the pressure was at such a high level, the pressure dependence of K_{IC} for polyethylene was insignificant [8]. In order to avoid environmental stress corrosion cracking, the specimen was separated from the pressure fluid by a thin rubber sheath in which a neutral medium of deionized water was added for transmitting the pressure to the surface of the specimen. After the system had achieved conditions of equilibrium pressure and temperature, a tensile load was applied to the specimen by the downward movement of the crosshead at a constant speed of 2 mm min^{-1}. The force on the specimen was detected by strain gauges on two rods connected to the crosshead, and subsequently recorded on a chart recorder. The testing machine was stopped immediately after crack growth initiation had been detected by a small change in the load–extension curve due to the small increase of compliance of the specimen. The fracture toughness value, K_{IC}, was then calculated using Equation 1

$$K_{\mathrm{IC}} = Y\sigma(\pi a)^{1/2} \qquad (1)$$

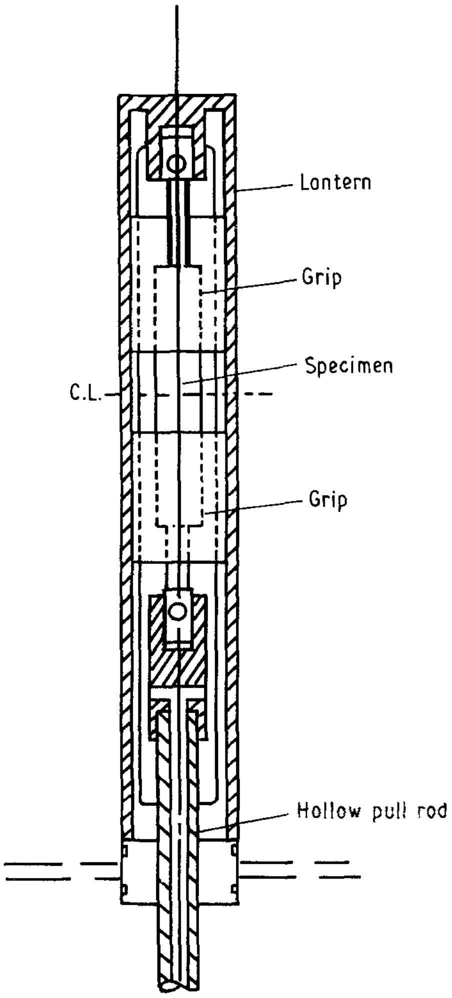

Figure 3 Detail of specimen holder.

where Y, σ and a are the geometry correction factor, applied stress at crack initiation and notch depth of the specimen, respectively. The geometry correction factor, Y, was calculated using the equation proposed for isotropic materials

$$Y(\pi)^{1/2} = 1.98+0.36(a/w)-2.12(a/w)^2+3.42(a/w)^3 \tag{2}$$

Sweeney *et al.* [8] evaluated the appropriate Y values for the oriented Hizex specimens by a complex finite-element method. Their results, and the values for Y calculated from Equation 2, agree with each other within experimental error.

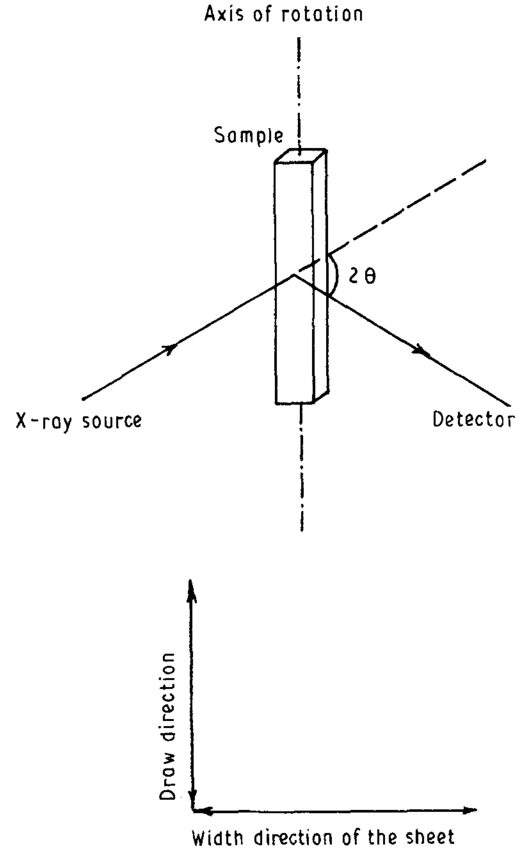

Figure 4 Schematic diagram of arrangement for X-ray diffraction measurements.

3.3. X-ray analysis

The crystallite orientation in the die-drawn specimens was determined by X-ray diffraction using a Siemens diffractometer. A longitudinal specimen at draw ratio 9.5:1 was prepared for each polymer. The length of the specimen was 40 mm. The width was the same as the original thickness of the drawn sheet (~ 3.0 mm). The specimen was positioned inside the diffractometer as shown in Fig. 4. The detector was positioned to maintain the diffraction angle, 2θ, at 24.0° for the (2 0 0) reflection using CuK_α radiation. The specimen was rotated about the vertical axis through 360° during the scan (ω-scan) about an axis perpendicular to this figure. The variation in intensity for the reflected X-ray beam was recorded. The diffraction angle was then changed to 36.4° for the (0 2 0) planes, and the experiment was repeated.

4. Results and discussion

4.1. High-pressure tensile testing

It is known that various grades of polyethylene have different die-drawing characteristics. Homopolymers of polyethylene can be drawn to high draw ratios, e.g. 25:1 for Rigidex 006-60. The maximum draw ratio which can be achieved in polyethylene copolymers is reduced by increasing the branch concentration [9] to about 20:1 and 10:1 for Rigidex 002-55 and Rigidex 002-40, respectively. These differing drawing characteristics can be reflected quantitatively by the fracture test results.

The high-pressure tensile test results for the polymers described in Table I are shown graphically in Figs 5–11, and summarized in Table II, together with the results for Hizex 7000F obtained by Sweeney *et al.* [8]. The high-pressure tensile testing results show that, as a result of orientation, there is a general increase in fracture toughness for these polymers except for the transverse specimens of the homopolymers Unifos 2912 and Rigidex 006-60, and the copolymer Rigidex R40 at draw ratio 9.5:1. The K_{IC} values for the longitudinal specimens at draw ratio 9.5:1 (~ 7.5:1 for Rigidex H060-45) were higher than those for 5:1, which like the accepted increase in longitudinal modulus can be primarily attributed to

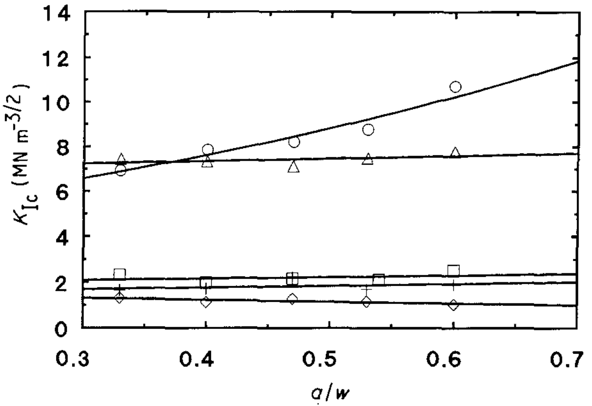

Figure 5 High-pressure tensile test results for Rigidex 006-60 ○ Longitudinal (DR9.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverse (DR9.5); +Isotropic.

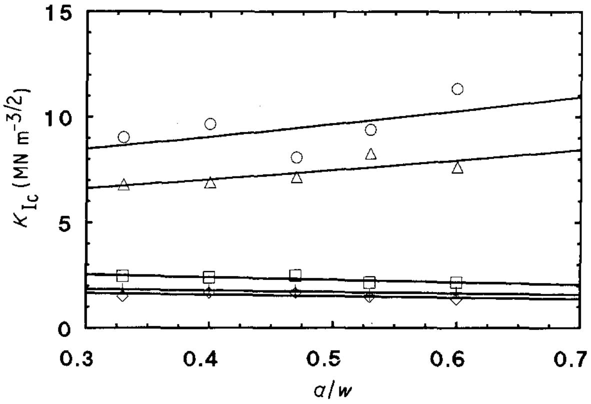

Figure 6 High-pressure tensile test results for Unifos 2912 ○ Longitudinal (DR9.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverse (DR9.5); +Isotropic.

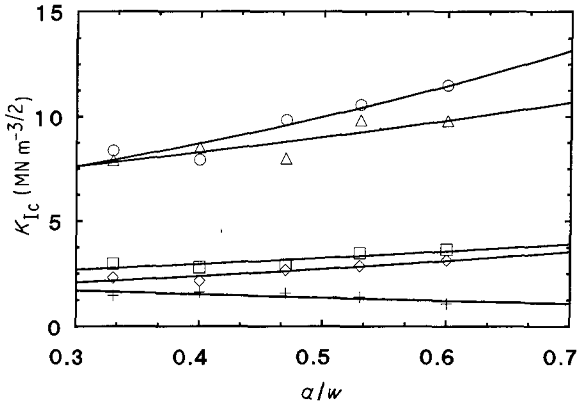

Figure 7 High-pressure tensile test results for Rigidex 002-55 ○ Longitudinal (DR9.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverse (DR9.5); +Isotropic.

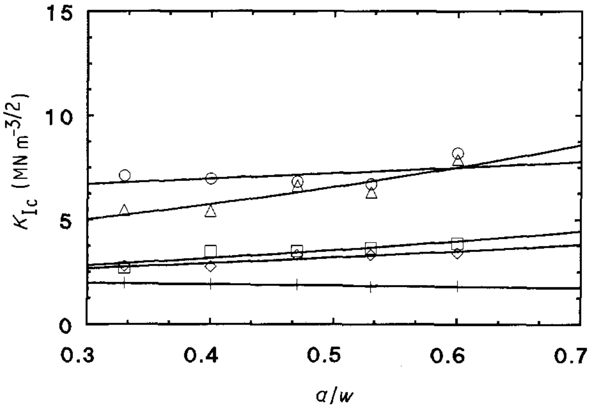

Figure 8 High-pressure tensile test results for Rigidex H060-45 ○ Longitudinal (DR7.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverse (DR7.5); +Isotropic.

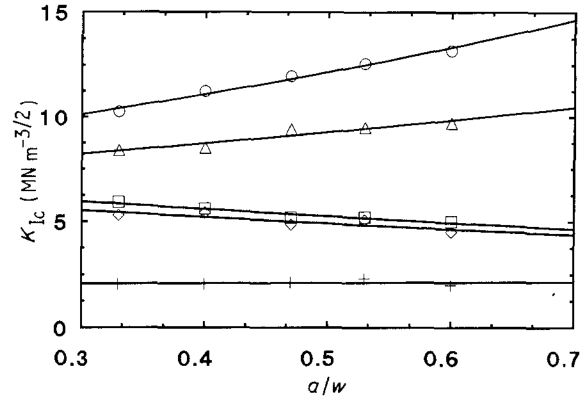

Figure 9 High-pressure tensile test results for Rigidex 002-40 ○ Longitudinal (DR9.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverso (DR9.5); +Isotropic.

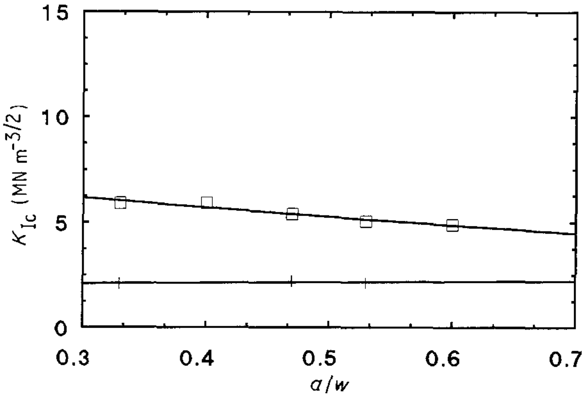

Figure 10 High-pressure tensile test results for TR-418 ○ Longitudinal (DR9.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverse (DR9.5); +Isotropic.

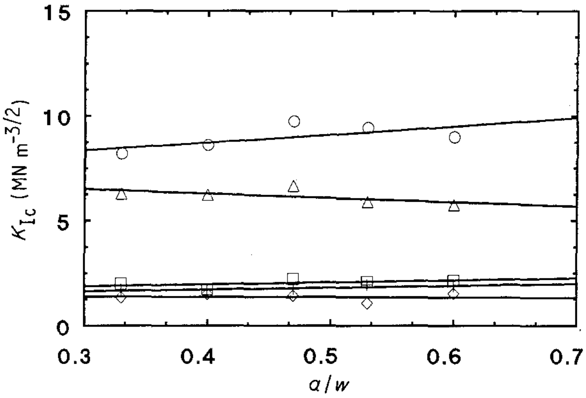

Figure 11 High-pressure tensile test results for Rigidex R40 ○ Longitudinal (DR9.5); △ Longitudinal (DR5); □ Transverse (DR5); ◇ Transverse (DR9.5); +Isotropic.

the higher extent of molecular orientation in the draw direction (the load axis in this test). By contrast, the K_{IC} values for transverse specimens were lower for draw ratio 9.5:1 compared with 5:1 materials.

Although the performance of polyethylenes can be enhanced greatly along the draw direction as a result of orientation, the fracture toughness in the transverse direction is also important because the latter represents the weakest direction for an oriented polymer. Therefore, we will pay particular attention to the transverse loading. Table I describes a range of polyethylene with various molecular weights and small side group content. By comparing their K_{IC} values selectively, the effect of these factors on the performance of polyethylene can be examined. The effect of short branches, e.g. *n*-butyl, on fracture toughness

TABLE II Summary of the high-pressure tensile test results for the polymers used in this research. The results for Hizex 7000F are quoted from [8]. DR = draw ratio

Grade	Average K_{IC} (MN $m^{-3/2}$)				
	Isotropic	Trans ~ 5:1	Long ~ 5:1	Trans ~ 9.5:1	Long ~ 9.5:1
Hizez	1.5 ± 0.1	Not tested	Not tested	4.6 ± 0.15	14.0 ± 1.0
006-60	1.8 ± 0.24	2.2 ± 0.26	7.0 ± 1.3	1.2 ± 0.16	8.0 ± 1.7
Unifos	1.7 ± 0.14	2.3 ± 0.31	7.3 ± 0.7	1.5 ± 0.21	9.5 ± 1.4
002-55	1.4 ± 0.23	3.2 ± 0.5	9.0 ± 1.2	2.7 ± 0.5	10.0 ± 1.5
H060-45	1.9 ± 0.19	3.4 ± 0.6	6.0 ± 1.0	3.1 ± 0.5 (DR ~ 7.5:1)	7.2 ± 0.9 (DR ~ 7.5:1)
002-40	2.1 ± 0.17	5.4 ± 0.4	9.1 ± 0.8	5.0 ± 0.4	12.0 ± 1.3
TR-418	2.1 ± 0.13	5.4 ± 0.5	Not tested	Not tested	Not tested
R40	1.8 ± 0.29	2.0 ± 0.29	6.2 ± 0.9	1.3 ± 0.4	8.9 ± 0.9

can be seen by comparing the high-pressure tensile testing results for the copolymers Rigidex 002-40 and Rigidex 002-55 and the homopolymer Unifos 2912. These polymers have similar molecular weights and have *n*-butyl branch concentrations of about 4, 1 and 0 per 1000 carbon atoms, respectively. It can be seen from Table II and Figs 12 and 13 that Rigidex 002-40 has the highest fracture toughness values at both draw ratios of 5:1 and 9.5:1, whilst the homopolymer Unifos 2912 has the lowest corresponding values. The fracture toughness values for copolymer Rigidex 002-55, which has an intermediate branch concentration, lie between those for the previous two polymers. All of these results reveal the effect of low concentrations of short branches on the enhancement of fracture toughness for polyethylene.

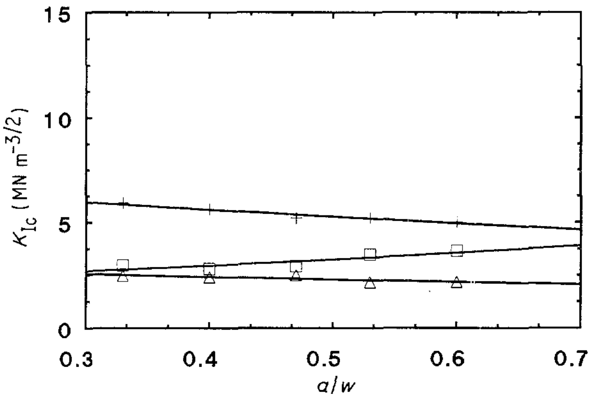

Figure 12 High-pressure tensile test results for the transverse specimens of (+) Rigidex 002-40, (□) Rigidex 002-55 and (△) Unifos 2912 at draw ratio 5:1.

The effect of molecular weight on the fracture behaviour of polyethylene can be studied by comparing the results for Rigidex 002-55 and Rigidex H060-45 at draw ratio 5:1. There is no direct comparison between these two polymers at draw ratio 9.5:1 because it was not possible to draw Rigidex H060-45 to such a high draw ratio. These two polymers have comparable *n*-butyl branch concentrations, but Rigidex H060-45 has a higher molecular weight than Rigidex 002-55 (Table I). However, in spite of the difference in molecular weight, their transverse fracture toughness values are comparable to each other (Fig. 14). A similar effect can also be seen by comparing the transverse results for homopolymers Unifos 2912 and its lower molecular weight counterpart Rigidex 006-60 (Figs 15 and 16). However, Sweeney *et al.* [8] found that the average K_{IC} values for their transverse specimens for the homopolymer Hizex 7000F at draw ratio 9.5:1 was 4.6 MN $m^{-3/2}$. This value is much higher than the corresponding ones for Unifos 2912 (1.5 MN $m^{-3/2}$) and Rigidex 006-60 (1.2 MN $m^{-3/2}$), and is comparable to that for the copolymer Rigidex 002-40 (5.0 MN $m^{-3/2}$). The improved performance for Hizex 7000F appears to be associated with its high molecular weight and/or its characteristic bimodal molecular weight distribution ($\bar{M}_n = 9600$; $\bar{M}_w = 282\,400$).

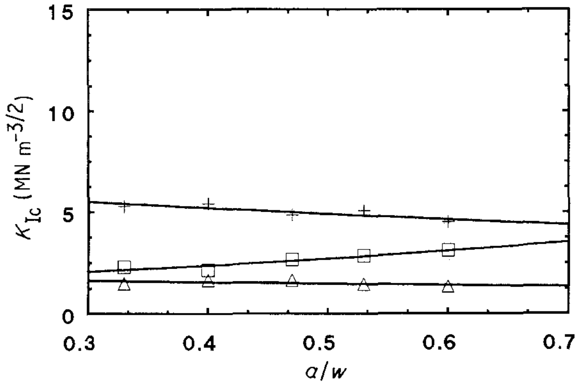

Figure 13 High-pressure tensile test results for the transverse specimens of (+) Rigidex 002-40, (□) Rigidex 002-55 and (△) Unifos 2912 at draw ratio 9.5:1.

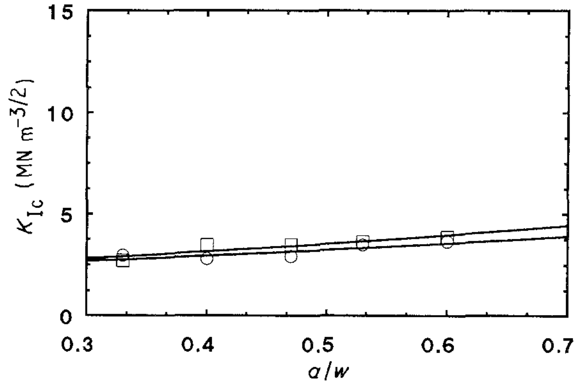

Figure 14 High-pressure tensile test results for the transverse specimens of (□) Rigidex 002-55 and (○) Rigidex H060-45 at draw ratio 5:1.

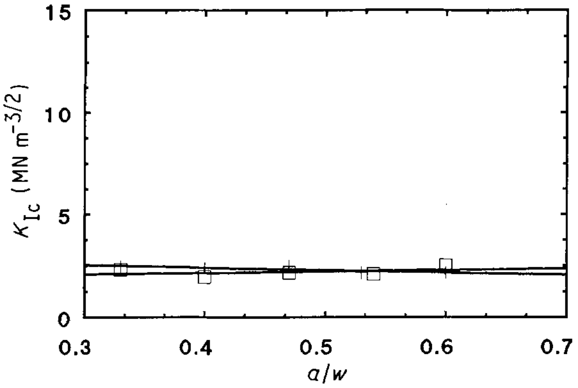

Figure 15 High-pressure tensile test results for the transverse specimens of (+) Unifos 2912 and (□) Rigidex 006-60 at draw ratio 5:1.

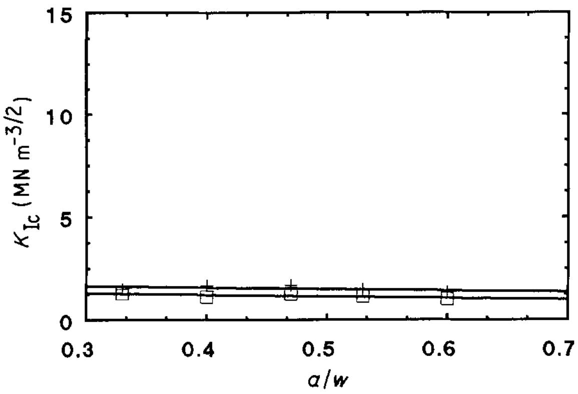

Figure 16 High-pressure tensile test results for the transverse specimens of (+) Unifos 2912 and (□) Rigidex 006-60 at draw ratio 9.5:1.

Capaccio and Ward [9] compared polyethylenes containing methyl branch groups with a homopolymer of similar molecular weight. They found that the drawing characteristics for their polymers were very similar to each other. It was believed that methyl branches could be incorporated into the crystal lattice to some extent [10]. The similarity of these polymers from the viewpoint of their mechanical properties is confirmed quantitatively by the high-pressure tensile testing results for the homopolymer Rigidex 006-60 and the copolymer Rigidex R40 with 5.6 methyl side groups per 1000 carbon atoms. The corresponding K_{IC} values for these two polymers are comparable to each other as shown in Table II and Figs 17 and 18.

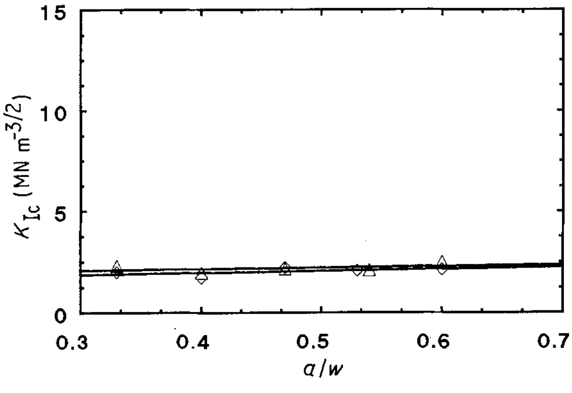

Figure 17 High-pressure tensile test results for the transverse specimens of (△) Rigidex 006-60 and (◇) Rigidex R40 at draw ratio 5:1.

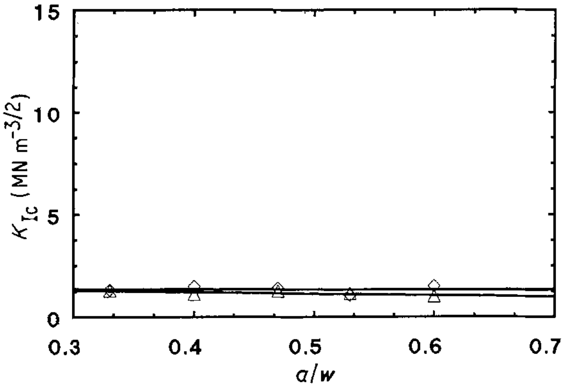

Figure 18 High-pressure tensile test results for the transverse specimens of (△) Rigidex 006-60 and (◇) Rigidex R40 at draw ratio 9.5:1.

The final comparison to be made is between copolymers TR-418 and Rigidex 002-40. TR-418 is a tough polyethylene on which only a few high-pressure tests have been performed so far. It can be seen in Fig. 19 that the K_{IC} values for these two polymers are almost identical, and in fact, their molecular characteristics are very similar to each other (Table I).

4.2. X-ray analysis

The high-pressure tensile test results show that factors such as molecular weight and short branches can affect the fracture toughness of polyethylene. It will be valuable to know the reasons for these changes. Sweeney *et al.* [8] have attempted to relate the fracture behaviour to the structure of their oriented Hizex 7000F specimens prepared by different die-drawing processes. They found that their sheet material, which was biaxially oriented, was twice as tough as their uniaxially oriented rod material. In view of this finding, X-ray scattering experiments were carried out to study the type of orientation in the die-drawn materials (draw ratio ~ 9.5:1) in this research, and the results are shown in Figs 20–25.

In their studies of the morphology of polyethylenes, Hay and Keller [11] described the texture of their oriented polymers as *b–c* sheets. These were prepared by elaborate drawing, rolling and annealing processes and were so called because they found that the crystallographic *b* and *c* axes lay preferentially in the plane of the sheets. A similar texture was also

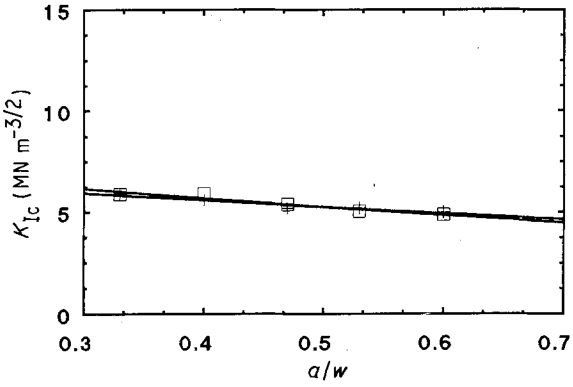

Figure 19 High-pressure tensile test results for the transverse specimens of (+) Rigidex 002-40 and (□) TR-418 at draw ratio 5:1.

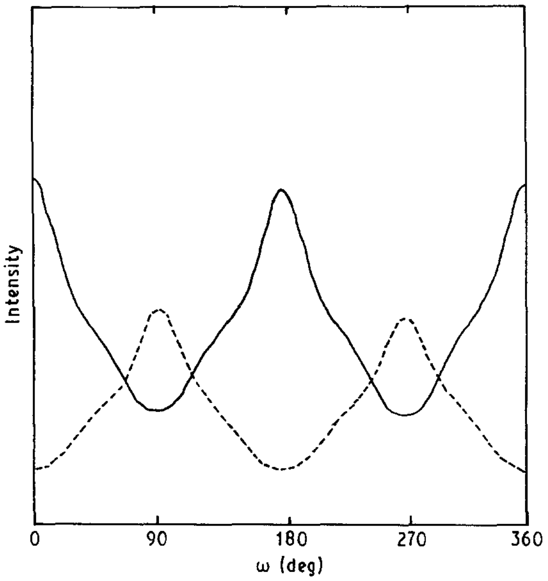

Figure 20 Diffractometer traces for the longitudinal specimen of Rigidex 006-60. The angle ω = 0° corresponds to the symmetric reflection orientation. (——) (2 0 0) reflection, (----) (0 2 0) reflection.

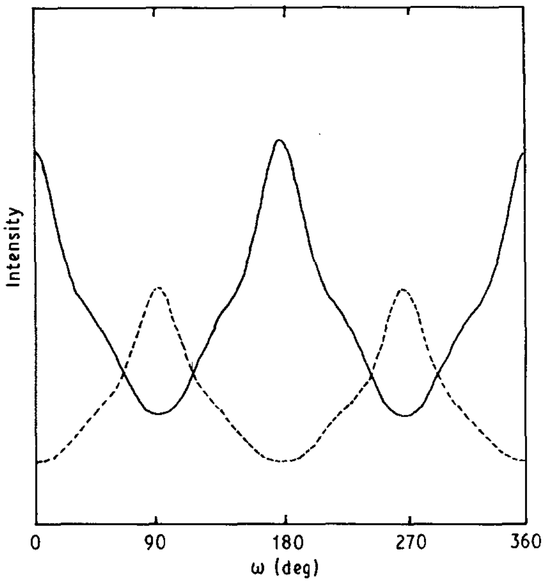

Figure 21 Diffractometer traces for the longitudinal specimen of Unifos 2912. The angle ω = 0° corresponds to the symmetric reflection orientation. (——) (2 0 0) reflection, (----) (0 2 0) reflection.

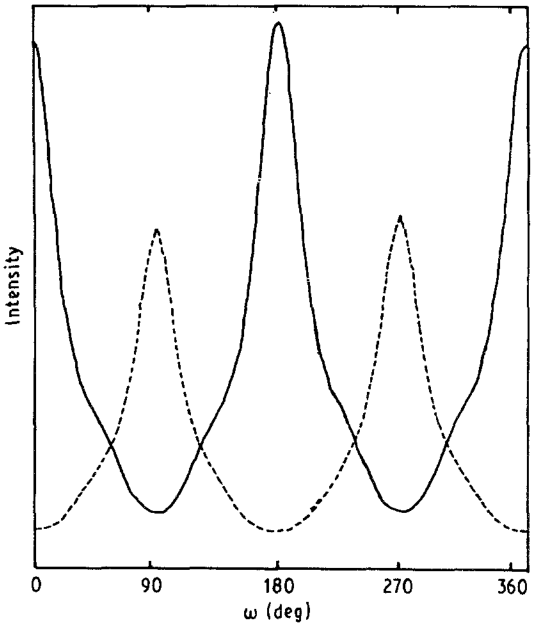

Figure 22 Diffractometer traces for the longitudinal specimen of Rigidex 002-55. The angle ω = 0° corresponds to the symmetric reflection orientation. (——) (2 0 0) reflection, (----) (0 2 0) reflection.

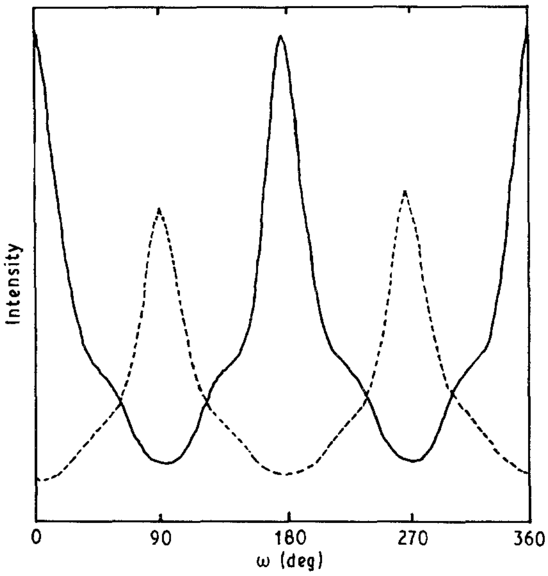

Figure 23 Diffractometer traces for the longitudinal specimen of Rigidex H060-45. The angle ω = 0° corresponds to the symmetric reflection orientation. (——) (2 0 0) reflection, (----) (0 2 0) reflection.

found by Sweeney *et al.* [8] in their die-drawn polyethylene sheet of Hizex 7000F at draw ratio 9.5:1. In this work, therefore, attention was particularly paid to the reflections from the (2 0 0) planes ($2\theta \sim 24.0°$) and the (0 2 0) planes ($2\theta \sim 36.4°$) because these two sets of planes are perpendicular to each other and contain the *b* and *c* axes, and the *a* and *c* axes of the orthorhombic unit cells of polyethylene, respectively.

In each curve in Figs 20–25, the orientation of the specimen at ω = 0° corresponds to the orientation for symmetric reflection from the plane of the sheet. Curves a and b are the traces of the ω-scans for the (2 0 0) and (0 2 0) reflections respectively. They resemble each other in shape, but their peaks are 90° out of phase. In each curve, the reflection intensity varies from its maximum to minimum or vice versa through a 90° rotation of the specimen. All these traces suggest that the (2 0 0) planes were preferentially oriented in the plane of the sheet in each case, and the (0 2 0) planes normal to the sheet, showing the so called *b–c* sheet texture.

The X-ray diffraction patterns show that all the materials at draw ratio 9.5:1 were biaxially oriented. Therefore, the variation in fracture behaviour for these polymers cannot be explained solely by their type of molecular orientation. It is necessary to consider their morphology in greater detail. Peterlin has proposed models for the plastic deformation of polyethylene and polypropylene in cold drawing [12]. He described the changes in morphology, from the plastic deformation of the original ductile spherulitic structure, to the

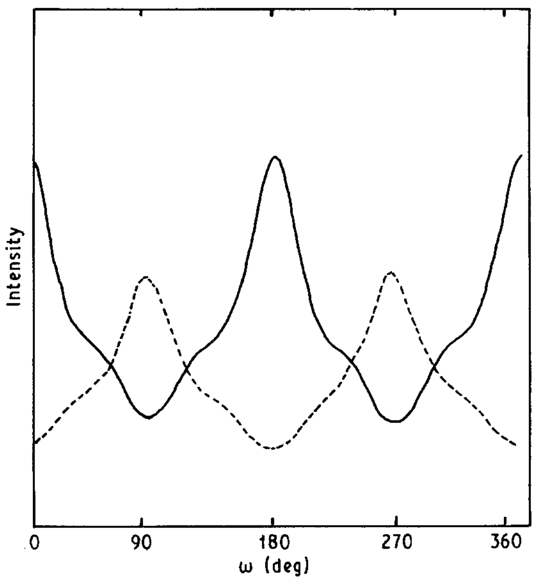

Figure 24 Diffractometer traces for the longitudinal specimen of Rigidex 002-40. The angle ω = 0° corresponds to the symmetric reflection orientation. (——) (200) reflection, (----) (020) reflection.

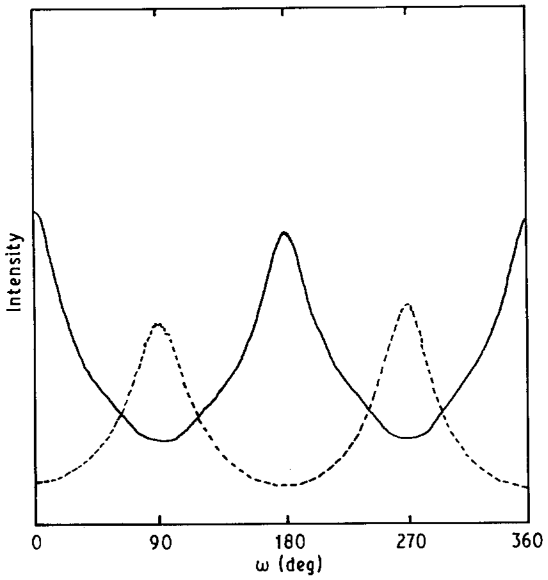

Figure 25 Diffractometer traces for the longitudinal specimen of Rigidex R40. The angle ω = 0° corresponds to the symmetric reflection orientation. (——) (200) reflection, (----) (020) reflection.

final strong fibrous structure with many tie molecules. Factors such as molecular weight and the nature and concentration of branches can change the morphology of polyethylene, e.g. the extent of physical entanglements by tie molecules. These changes can be accentuated and become more prominent after die-drawing to high ratios to give a wide range of mechanical properties.

It is remarkable that the fracture toughness values of the oriented Rigidex 002-40 and Hizex 7000F are so similar. This suggests that similar morphologies may be produced either by suitable distributions of short branches or molecular weight. It is therefore evident that morphological studies will be essential to a proper understanding of the fracture behaviour. Further work on morphology has been initiated and it is hoped to present the results in a subsequent publication.

5. Conclusions

The K_{IC} values for a range of oriented polyethylenes have been carefully compared. It was found that the oriented specimens with *n*-butyl side groups had higher K_{IC} values than their corresponding homopolymer counterparts despite the comparable fracture toughness of all these polymers in their isotropic state. This enhanced performance attributed to the effects of short branches was not observed in the copolymer Rigidex R40 with methyl side groups, which it is believed can be incorporated into the crystal lattice and, therefore, do not cause major changes in morphological structure. It is suggested that the high K_{IC} values for the oriented Hizex 7000F compared with Unifos 2912 and Rigidex 006-60 are due to a combination of a high weight-average molecular weight and a bimodal molecular weight distribution.

The X-ray analysis showed that all the specimens at draw ratio 9.5:1 had the so-called *b–c* sheet texture. Although biaxial orientation may be important in determining fracture toughness, it is clear from the differences between polymers of different chemical compositions that there will be considerable value in pursuing morphological studies of these very remarkable materials.

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