Fracture Mechanics of Polypropylene: Effect of Molecular Characteristics, Crystallization Conditions, and Annealing on Morphology and Impact Performance

A. O. IBHADON

Department of Chemistry, University College Scarborough, Filey Road, Scarborough, England YO11 3AZ, United Kingdom

ABSTRACT: Fracture mechanics study of polypropylene samples of various molecular weight, obtained under different crystallizations conditions, is reported. Fracture toughness values obtained at high speed of impact as well as at low temperatures increased with increasing molecular weight and decreasing crystallization temperature. Scanning electron micrographs of fractured samples aided in elucidating the fracture mechanism of the polymer studied. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2657–2661, 1998

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INTRODUCTION AND THEORY

A number of theories of fracture have been postulated over the years to explain the deformation behavior of polymers. This article summarizes the major points of the Grifith and Irwin models as applied to the deformation and fracture of polymers.[1–3]

Grifith considered that fracture produces a new surface area, and that for fracture to occur, the increase in energy required to create the new surface must be balanced by a decrease in elastically stored energy in the sample. To explain the large discrepancy between the measured strength of materials and that based on theoretical considerations, he postulated that the elastically stored energy is not distributed uniformly throughout the specimen or sample, but is concentrated in the neighborhood of small cracks. Fracture occurs due to these cracks which originate from preexisting flaws.

The growth of any crack is usually associated with an amount of work, dW, being done on the system by external forces and a change, dU, in the elastically stored energy, U. The difference between these quantities, $dW - dU$, is the energy available for the formation of a new surface.

A crack of length, dc, grows when,

$$dW/dc - dU/dc \geq \gamma dA/dc \qquad (1)$$

where γ is the surface free energy per unit area of surface and, dA, the associated increament of surface. If there is no change in the overall extension when the crack propagates, $dW = 0$ and,

$$-(dU/dc) \geq \sigma_B dA/dc \qquad (2)$$

The first term of this equation is a positive quantity.

Equation (2) allows the fracture stress, σ_B, of a material to be defined in terms of the crack length, c, by the relationship

$$\sigma_B = (2\gamma E^*/\pi c)^{1/2} \qquad (3)$$

E^* is equal to the Young's modulus, E, for a thin sheet under plane stress conditions and to $E/(1 - v^2)$, where v is the poisson ratio for a thick sheet in plain strain conditions.

Linear elastic fracture mechanics, LEFM, approach, with some modification, has been used with a high degree of success in explaining the fracture behavior of polymeric systems, whether these be semicrystalline polymers or toughened rubbers.[4-6] It is generally agreed that in semicrystalline systems the spherulite architecture plays a major role in altering the fracture behavior of these polymers.

Generally, an increase in spherulite size has been observed to alter the mechanical behavior of polymers such as PP and PE. Tensile properties such as yield stress, elongation at break, and modulus decrease with increased spherulite size. This is attributed to impurity segragation at the spherulite boundaries, the regions from where fracture is initiated and propagated. However, how the spherulitic morphology controls crack initiation, growth, and crack propagation mechanisms in these materials is not completely clear.

For an infinite sheet with a central crack of length, c, subjected to a uniform stress σ, Irwin showed that

$$K_1 = \sigma(\pi c)^{1/2} \tag{4}$$

Irwin postulated that when σ reaches the fracture stress, σ_B, K_1 has a critical value given by

$$K_1 c = B(c)^{1/2} \tag{5}$$

The fracture toughness of the material can then be defined by the value of $K_1 c$, called the critical stress intensity factor which defines the stress field at fracture. Equation (5) can be written as

$$\sigma_B = (K_1^2 c/\pi c)^{1/2} \tag{6}$$

which is identical in form to eq. (3), which is Griffith's formulation. The strain energy release rate is the energy available for a unit increase in crack length

$$G = dW/dA - dU/dA$$
$$= 1/V[dW/dc - dU/dc] \tag{7}$$

where W and A have their usual meaning, and B is the thickness of the specimen. Fracture occurs when G reaches a critical value Gc,

$$G = Gc \tag{8}$$

and Gc is equal to 2γ in Grifith formulation. The critical strain energy release rate, Gc, can be determined directly by combining a load-extension plot from a tensometer with the determination of the movement of the crack across the specimen or sample and noting the load for a given crack length. On the other hand, test pieces of standard geometry can be used for which the compliance is known as a function of crack length.

In this study, LEFM approach has been used to study the relationship between the critical strain energy release rate, Gc, the critical stress intensity factor, Kc, and the molecular weight of PP samples. Part of the information that could be obtained from this study is the influence of the spherulitic morphology on the fracture mechanism of polymer samples.

EXPERIMENTAL

Commercial samples of isotactic polypropylene (SH, Shell PP, and BS, British Sidac PP) used in this study had the following characteristics. The molecular weight ranged from 10^5 to 10^6, the density from 900–935 kg/m^3, and crystallinity from 15 to 53%. Samples were obtained from commercial iPP manufacturers in the United Kingdom.

Flat sheets of 5 mm thickness were obtained by pressing the material in a hydraulic press maintained at 200°C. The samples were allowed to remain in the press for about 10 min, after which the press was released and the materials immersed in a thermostated bath. This treatment resulted in the formation of different spherulitic architectures in the samples. After the thermostated bath treatment, the samples were quenched rapidly in ice-cold water. The degree of crystallinity and melting temperatures were measured at a scanning rate of 5 K per min using a model DSC-2 interfaced to a microprocessor for data collection and analysis. Effect of orientation on fracture toughness was carried out by cutting specimens from annealed samples at various angles of orientation. In the figures that follow, closed symbols represent Shell iPP, while open symbols represent British Sidac iPP.

Scanning Electron Microscopy

Microtomed samples were examined using a Cambridge 600 SEM. Samples were etched in a satu-
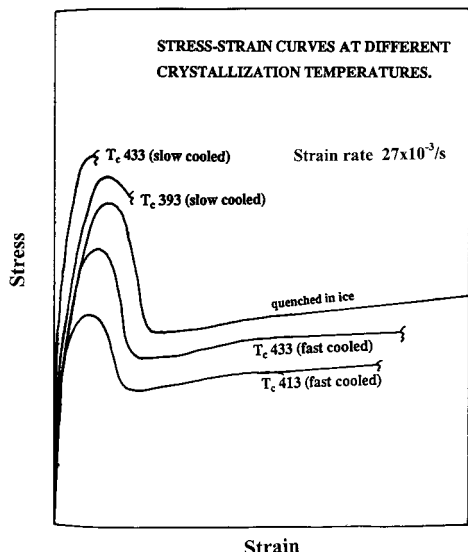
Figure 1 Stress strain profiles of iPP at different crystallization temperatures.

rated solution of either CrO_3/H_2SO_4 or $CrO_3/$ HNO_3. Fracture tests were carried out in a Charpy Instrumented Impact Tester. The speed of impact was kept at 1 m/s. Fracture surfaces of notched specimens were examined using the SEM after the surfaces of the samples were coated with a thin layer of gold/palladium alloy.

RESULTS AND DISCUSSION

The stress–strain curves of specimens crystallized at various crystallization temperatures and cooling conditions is shown in Figure 1. The sample, which crystallized at 393 K by slow cooling from the melt, had a spherulite diameter of 120 μ while at the same crystallization temperature, but on fast cooling, there was a decrease in spherulite diameter to 90 μ. This suggests that the spherulite size obtained on crystallization depends more on the rate of cooling than on the temperature at which crystallization was carried out. Thus slow cooling rates results in large spherulites and brittle fractures, while fast cooling rates results in smaller spherulites and ductile fractures.

The plot of yield stress against spherulite size, Figure 2, shows an increase of yield stress with increased spherulite size. This was followed by a decreased yield stress as the spherulite size increased to about 100 μ in diameter. Above this size, specimens deformed in a brittle mode,

whereas below this size, deformation was essentially ductile and was accompanied by an increase in elongation at break and decreasing yield stress. For specimens that deformed in a ductile manner, the yield stress increased with increasing strain rate at a given spherulite size. Similar results have been obtained for other polymeric systems.[7–10] For completely brittle fractures, the yield stress is the fracture stress because the load extension plots have no linear elastic region. Samples with large spherulite sizes exhibited brittle deformation because the yield stress was probably above the crazing stress.

Thus, the major factor controlling the fracture mechanism of the polymer samples seem to be the spherulitic morphology. The observed deformation characteristics are, therefore, attributed generally to impurity segregation into the spherulite boundaries, sample shrinkage, and void formation during crystallization. This results from differences in cooling rates and crystallization temperatures resulting in differences in spherulitic morphology.

The critical strain energy release rate, Gc, obtained from plots of the energy absorbed at fracture, W (or U), against $Bd\phi$ (Fig. 3), showed an increase of Gc with increasing molecular weight over a wide crystallization range (closed symbols represent Shell iPP—higher molecular weight) while open symbols represent British Sidac iPP—lower molecular weight). In addition, for samples of the same molecular weight, Gc decreases with increasing crystallization temperature. This was also the case with the stress intensity factor, Kc. Gc, however, increased with increased reciprocal thickness. These results indicate that both Gc and Kc are
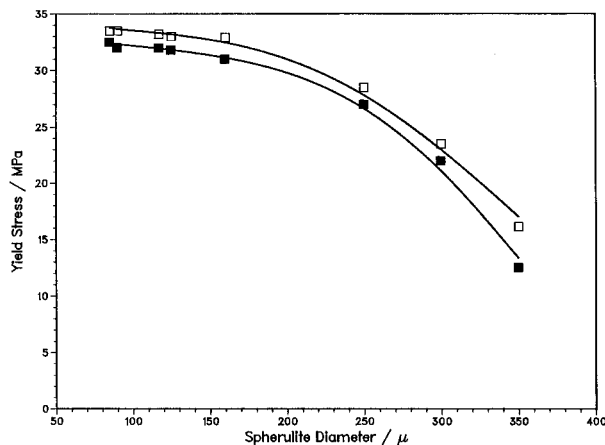

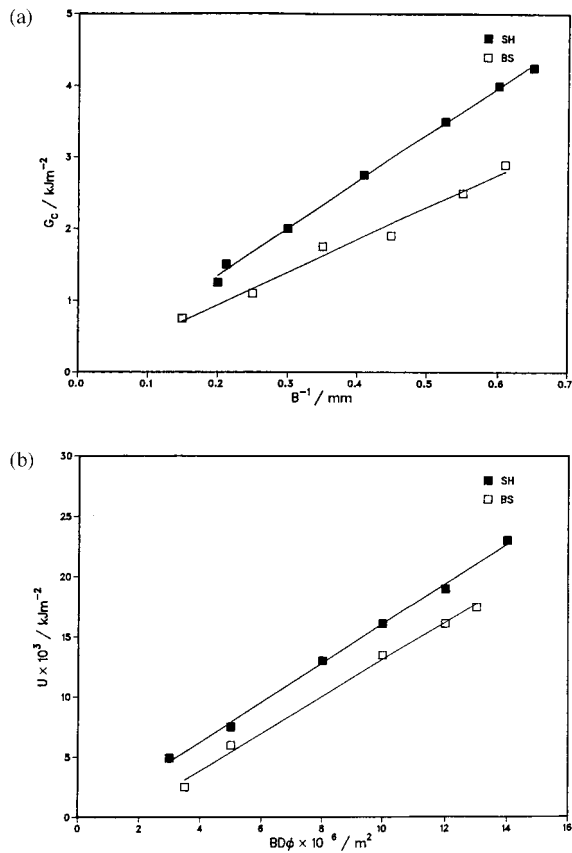**Figure 2** Yield stress as a function of spherulite size.

Figure 3 (a) G_c as a function of reciprocal thickness; (b) energy as a function of $BD\phi$.

dependent not only on the molecular characteristics of the sample but also on the temperature at which crystallization was carried out.

The annealing treatments carried out on the already crystallized samples resulted in the enhancement of the fracture parameter values. Thus, Kc and Gc can be used to monitor the molecular changes in bulk crystallized PP samples induced by different heat treatments and molecular weight. Values of Gc and Kc could be connected with material morphology in terms of resistance to crack growth and propagation by the spherulitic microstructure.[11,12]

The plot of the fracture toughness as a function of the angle of orientation of annealed samples is shown in Figure 4, from where it can be seen that the fracture toughness increased for deformation that occurred perpendicular to the draw direction (cleavage perpendicular to the draw direction) and decreased for deformation that occurred parallel to the draw direction. This is attributed to the alignment of covalent bonds within the chains

parallel to the orientation direction of annealed samples. If the applied stress is parallel to the orientation direction, then craze initiation, growth, and subsebsequent breakdown and craze extension are inhibited and only occur at higher stress levels than in the isotropic material. On the other hand, if the applied stress is perpendicular to the orientation direction, crack breakdown and extension will occur readily.

Spherulite Architecture

The spherulites obtained for deformed oriented samples were practically undeformed. This is similar to the situation that was obtained at high crystallization temperatures. At high crystallization temperatures, the interspherulitic regions are weak because of few molecular interconnections. They act as effective sites and easy fracture pathways. The contribution to the fracture toughness is determined by the energy required to strain and break these interconnections, and unlike the high fracture values obtained for oriented samples, low fracture toughness values are obtained in this case.[13-15]

Features observed in the SEM micrographs of fully spherulitic samples revealed the presence of a well-defined plastic zone. The presence of this zone suggests that the precursor to crack growth is the formation of a large number of crazes. The crazes develop and propagate within the spherulitic and interspherulitic regions. When they break down, cracks are formed. However, at low crystallization temperatures, the degree of spherulitic interconnection is sufficiently high to sustain large deformation before fracture finally occurs. Thus, the higher Kc and Gc values obtained
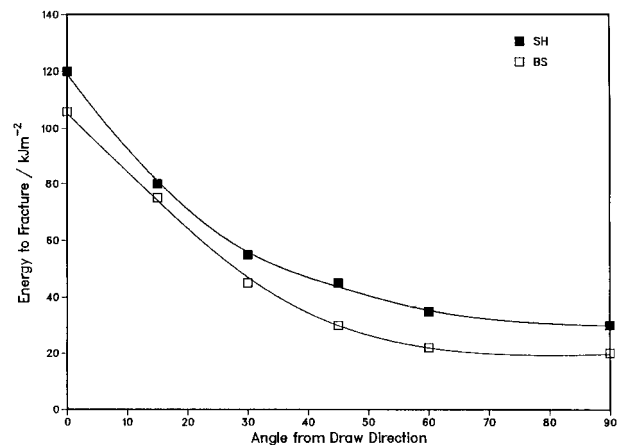

Figure 4 Effect of orientation on fracture toughness.

in the highly spherulitic samples results from larger energy absorption due to the presence of crazes and the crazing mechanism.

The plastic deformation that occurs at the crack tip is coarse, and the fine spherulitic morphology can be modified by changing the molecular weight. A higher degree of plastic deformation occurs in the spherulitic boundary when the molecular weight of the material is increased. This might be due to the fact that with an increase in molecular weight, the entanglement density due to interlayered amorphous material is enhanced. This results in an improved impact performance with molecular weight. Because the crazed area near the notch tip is greater the higher the molecular weight, the resistance to deformation of the interspherulitic and intraspherulitic link density increases and, hence, the improved fracture toughness observed.

CONCLUSION

This study investigated the effect of molecular weight and spherulitic morphology on the fracture behavior of isotactic polypropylene samples. The results suggest that the fracture behavior of the polymer, that is, crack initiation and growth, as well their breakdown, is controlled by the interconnections within the material, and these determine the structure of the crazes that are formed. These interconnections are increased by annealing treatments as melting and recrystallization occur within these regions. This would eventually lead to improved resistance to crack propagation and, hence, greater toughness. Differences in crystallization conditions affect the spherulitic morphology obtained.

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