Fracture Toughness of Phenolphthalein Polyether Ketone

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SYNOPSIS

The static and impact fracture toughness of phenolphthalein polyether ketone (PEK-C) were studied at different temperatures. The static fracture toughness of PEK-C was evaluated via the linear elastic fracture mechanics (LEFM) and the J-integral analysis. Impact fracture toughness was also analyzed using the LEFM approach. Temperature and strain rate effects on the fracture toughness were also studied. The enhancement in static fracture toughness at 70°C was thought to be caused by plastic crack tip blunting. The increase in impact fracture toughness with temperature was attributed two different mechanisms, namely, the relaxation process in a relatively low temperature and thermal blunting of the crack tip at higher temperature. The temperature-dependent fracture toughness data obtained in static tests could be horizontally shifted to match roughly the data for impact tests, indicating the existence of a time–temperature equivalence relationship. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Linear elastic fracture mechanics (LEFM) is now widely used to characterize fracture behavior of polymeric materials.[1] The size and geometry-independent parameters, K_{IC} and G_{IC}, have been proven to represent true material constants of most glassy polymers, provided that certain restrictive size criteria of the testing specimen have been satisfied[2] to meet the requirements of plane–strain fracture.

The stress intensity factor K_{IC} is calculated by the equation

$$K_{IC} = 1.5Y(PL/BW^2)a^{1/2} \quad (1)$$

where K_{IC} = fracture toughness, Y = shape factor (see below), L = distance between span supports, P = load at fracture, B = specimen thickness, W = specimen width, and a = crack depth.

The shape factor Y is a function of the (a/W) ratio, in this case, Y is given by

$$Y = 1.93 - 3.07(a/W) + 14.53(a/W)^2 - 25.11(a/W)^3 + 25.80(a/W)^4. \quad (2)$$

In eq. (1), if we keep L, B, W, and a the same, the average of a set of experiments will give K_{IC}.

However, for the toughest polymers, valid measurements were restricted to low temperatures. At higher temperatures, extensive plasticity occurred at the crack tip, invalidating the use of LEFM. It was suggested that, under such conditions, other methods that take into account the plasticity at the crack tip, such as the J-integral, may have to be used.

The J-integral analysis was first proposed by Rice.[3] The experimental procedure to determine the critical J-integral, J_{IC}, was later suggested by Begley and Landes by construction of the crack growth resistance curve and crack blunting line.[4,5] Physically, the J-integral can be considered as the difference of the potential energy between two loaded identical bodies with slightly different crack lengths, i.e.,

$$J = \frac{1}{B}\frac{dU}{da} \quad (3)$$

where B is the thickness of the loaded body, U is the total potential energy obtained by measuring the

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area under the load-displacement curve, and a is the crack length. Sumpter and Turner later expanded the above equation and rewrote it as[6]

$$J = J_e + J_p \tag{4}$$

$$J = \frac{\eta_e U_e}{B(W-a)} + \frac{\eta_p U_p}{B(W-a)} \tag{5}$$

where J_e and J_p are the elastic and plastic components of the total J, respectively, and η_e and η_p are elastic and plastic factors corresponding to J_e and J_p. $(W-a)$ is the ligament length. In notched-bend specimens, when $0.4 < a/W < 0.6$ both η_e and η_p are equal to 2 and eq. (3) is simplified to

$$J = \frac{2U}{B(W-a)}. \tag{6}$$

The procedure for J_{IC} determination has been standardized by ASTM E813-81.[7] In ASTM E813-81 the $J - \Delta a$ data points used to construct a $J - R$ curve are those points located between two exclusion lines parallel to the blunting line (specified by $J = 2\Delta a\sigma_y$, σ_y is the yield stress) at crack growth $\Delta a = 0.006(W-a)$ and $\Delta a = 0.06(W-a)$, respectively. The valid data points are then linearly regressed to obtain the $J - R$ curve and the crack initiation point is defined as the intersection of the $J - R$ curve with the blunting line, which gives J_{IC}.

Many polymers are designed to satisfy the increasing demands of high toughness at low temperatures and high strain rates.[8–10] Therefore, to characterize the toughness under impact conditions is particularly important. The conventional Charpy and Izod impact tests measure the total energy required for breaking a standard notched bar and the apparent surface fracture energy is then obtained by dividing the total energy over the ligament area. Unlike the critical potential energy release rate, G_{IC}, or J-integral, J_{IC}, the apparent surface fracture energy is normally not reproducible, is specimen geometry and size dependent, and varies with the testing method.

Analysis of impact energy data based on LEFM was derived by Marshall et al.[11] and Brown.[12] The impact toughness, in terms of G_{IC}, of an elastically fractured material can be successfully evaluated by breaking a series of specimens with different initial crack lengths. The impact fracture energy, U, measured is related to G_{IC} by[11]

$$U = G_{IC}BW\phi(a/W) + U_k \tag{7}$$

where a is the initial crack length, B and W are the thickness and width of the specimen, respectively, and U_k is the kinetic energy loss. The correction factor, ϕ, is a function of a/W to account for geometry effects. ϕ is a dimensionless factor given by

$$\phi = \frac{C}{dC/d(a/W)} \tag{8}$$

where C is compliance.

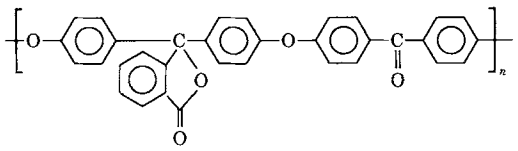
Equation (8) can be rewritten as follows[13]:

$$\phi = \frac{1}{2}\frac{a}{W} + \frac{1}{18}\frac{L}{W}\frac{1}{(a/W)}. \tag{9}$$

ϕ values were calculated from eq. (9).

Thus when U is plot against $BW\phi$, a straight line with G_{IC} as the slope and U_k as the intercept can be obtained.

This study focused on phenolphthalein polyether ketone (PEK-C),



which is an amorphous polymer with a high T_g, that can be used as an engineering thermoplastics and matrix of composites. Because PEK-C is being increasingly used in engineering applications, there is a need to understand temperature effect on fracture toughness.

EXPERIMENTAL

Material and Specimen Preparation

The material used in this study was PEK-C supplied by Xu Zhou Engineering Plastics Co. China in the powder form (its reduced viscosity in chloroform at a temperature of 25°C is 0.50 dL/g; its yield stress, σ_y; Young's modulus, E, and Poisson's ratio, υ, at different temperatures are shown in Table I). The original powders were dried at 120°C for 1 day and then were extruded at 330–350°C in an SHJ-30 twin-screw extruder and pelletized. The pellets were dried at 120°C for 1 day and then were injection molded into required specimens on a JSW-17SA injection-molding machine (Japan) with barrel temperatures of 325–360°C.

The Charpy impact specimens were injection-molded bars 15-mm wide, 10-mm thick, and 120-

Table I E, v, σ_y, K_{IC}, and J_{IC} of PEK-C as a Function of Temperature

T (°C)	E (GPa)	v	σ_y (MPa)	K_{IC} (MPa $m^{1/2}$)	J_{IC} (kJ/m^2)
12	2.29	0.366	96.01	2.34	1.80[a]
40	1.98	0.368	89.04	2.56	2.47[a]
70	1.72	0.371	84.02	2.66	3.06[a]
100			71.12		2.17
120			59.83		2.70
140			55.75		2.88
160			46.78		3.55
190			31.60		3.75

[a] Obtained according to eq. (10).

mm long. All specimens were subsequently notches in the midspan and were sharpened further with a razor blade. To avoid plastic deformation at the crack tip, the razor blade should always be fresh and the pushing speed as slow as practical. The normalized crack length (a/W) of the specimens were varied from 0.2 to 0.8.

The dimensions of the single-edge notched three-point bending (SENB) specimens for the K_{IC} and J-integral tests were 8 × 16 × 80 mm. A deep notch with a/W = 0.5 was made in the center of one side of the test bars with the same method described above.

Mechanical Tests

Charpy impact tests were performed on a JJ-20 Model Instrumented Impact Tester with single-edge notched specimens in the temperature range 15–240°C. The span L was 70 mm and the striking velocity was 3.8 m/s. During the tests, specimens with different initial crack lengths were heated in an oven to the temperature required for at least 20 min in order to reach the thermal equilibrium. The specimens were then quickly mounted on the specimen holder and impacted immediately. The impact fracture energy was taken directly from the computer. The initial crack length, a, was measured using a traveling microscope on the fractured specimen of the test.

To study K_{IC} of fracture, static SENB tests were carried out on an Instron test machine (Instron 1121) at a constant crosshead speed of 5 mm/min in the temperature range 12–70°C. A span-to-width ratio of 4 was used. A set of specimens with identical initial crack lengths were loaded until total failure occurred. The load vs. displacement curves were recorded.

J-integral tests were conducted on SENB geometry with multiple specimens on the same Instron 1121 with the same crosshead speed and at five different temperatures, 100, 120, 140, 160, and 190°C. When the load-displacement curve reached a certain position where a required crack extension was obtained, the specimens were unloaded, immersed in liquid nitrogen for 20 min, and subsequently separated quickly with a hammer and wedge. The length of the stress-whitening zone between the end of the notch and the commencement of the fast fracture was considered as the true crack extension measured by a traveling microscope.

RESULTS AND DISCUSSION

K_{IC} and J-Integral Tests

In the temperature range from 12 to 70°C, the material exhibited brittle fracture behavior and it gave valid LEFM data, so we used K_{IC} to describe its fracture behavior. The values of K_{IC} at different temperatures were calculated using eqs. (1) and (2) and were converted to G_{IC} and J_{IC} by the following relation

$$J_{IC} = G_{IC} = \frac{K_{IC}^2(1 - v^2)}{E} \tag{10}$$

where E is the elastic modulus and v is the Poisson's ratio. The results are listed in Table I.

With increasing temperature (from 100 to 190°C), the material became more ductile so LEFM was invalid. Another J-integral method was used. The value of J for each specimen was calculated using eq. (6). Figure 1 shows the result at 100°C plotted on a single graph as J vs. Δa. Also shown in the same figure are the blunting line ($J = 2\Delta a\sigma_y$), two

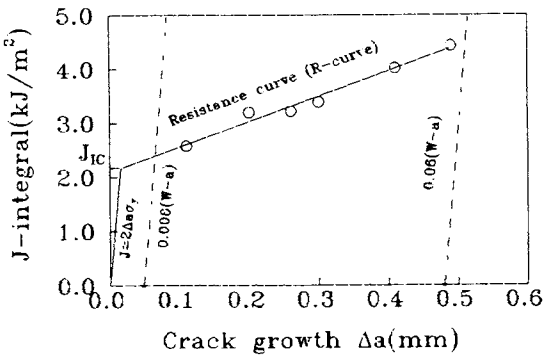


Figure 1 Schematic J-integral crack extension, Δa, curve at 100°C.

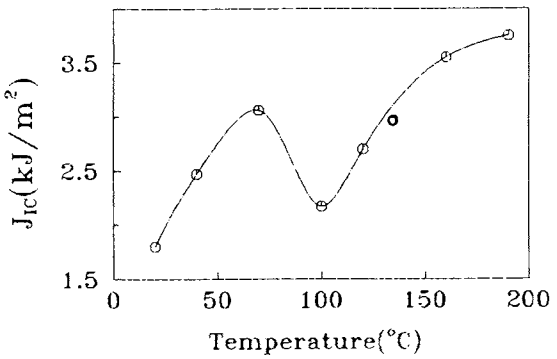


Figure 2 Temperature dependence of J_{IC}.

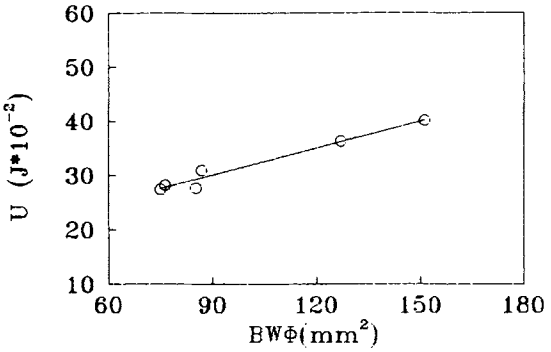


Figure 3 U vs. $BW\phi$ for PEK-C at 240°C.

exclusion lines parallel to the blunting line at the crack growth $\Delta a = 0.006(W - a)$ and $\Delta a = 0.06(W - a)$, and the least square fitted line to the crack extension points. J_{IC} is determined at the intersection of the $J - R$ curve with the blunting line. The J_{IC} values for PEK-C at other temperatures is obtained by the same method (Table I) and the temperature dependence of J_{IC} of PEK-C is shown in Figure 2. From Figure 2 we can see that there is a peak fracture toughness at about 70°C. This phenomenon occurs when the temperature approaches T_β of the polymer, then the β-relaxation process becomes active and absorbs considerable energy. This relaxation process results in localized plastic blunting of the crack tip that leads to a dramatic increase in toughness as shown in Figure 2.

Charpy Impact Tests

The Charpy impact results at different temperatures were analyzed with eq. (7). A representative G_{IC} plot is shown in Figure 3. Plot of U vs. $BW\phi$ and G_{IC} was determined from the slope of the curve. Linear regression was used to calculate the slope. The G_{IC} data for PEK-C at different temperatures calculated from such plots are plotted in Figure 4. Briefly, G_{IC} is constant from 15 to 70°C, increases slightly at 100°C, rises dramatically at 180°C, and then drops down.

The temperature effect on the impact fracture toughness of polymeric materials has received a good deal of attention in the past.[14-20] Much of the work has been concentrated on the question of whether or not the molecular relaxation processes occurring in a polymer have a one-to-one correlation with the energy absorption mechanism observed in the mechanical tests. Although the answer to this question is still far from settled, with the aid of previous work, the experimental observations of the present study are not very difficult to understand. As pointed out in a previous article, there are three factors that are of particular importance when the temperature effect on the impact behavior is considered, i.e., the tan δ loss, dynamic effects, and the crack tip thermal blunting caused by adiabatic heating induced by the high strain rate in an impact test.

Many authors have considered the possibility that the impact fracture toughness of polymers can be related to the presence of viscoelastic relaxations or damping as observed in dynamic mechanical or other tests.[21-23] The understanding of such correlations has important implications for the development of high impact toughness polymers. By considering impact failure and viscoelastic relaxation data as a function of temperature for a variety of polymers, Heijboer[21] made several observations. In some polymers [e.g., poly(tetrafluoroethylene)], there are viscoelastic relaxations that qualitatively correlate with high impact toughness. The qualitative correlation comes from observations of peaks in the temperature-dependent viscoelasticity and impact data that appear near each other. A secondary transition provides a mechanism for dissipating energy, and so would be expected to increase the strain energy release rate, G_{IC}. According to our dynamic mechanical study of PEK-C, it is found that there is a β-transition loss

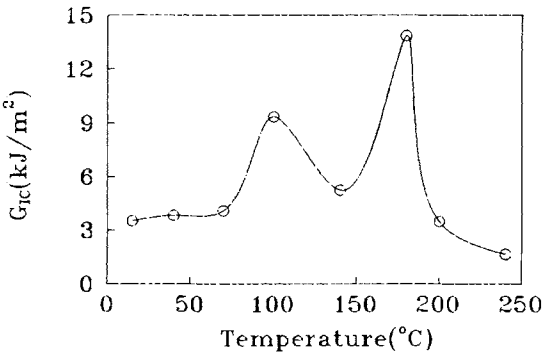


Figure 4 G_{IC} of PEK-C vs. temperature.

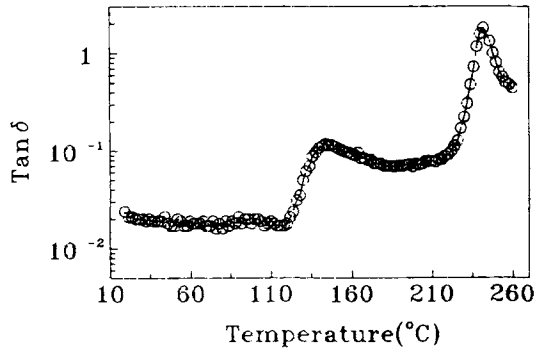


Figure 5 Temperature dependence of tan δ curve PEK-C at 3.5 Hz.

process with a peak at about 140°C (Fig. 5). The peak in G_{IC} vs. the temperature curve is about 100°C, which is not exactly the same as the tan δ loss. The reason is that the impact tests and the viscoelastic experiments were done under different conditions. The impact tests were done with standard impact testing equipment, and the relaxation tests were typically done with standard dynamic mechanical experiments. The different testing configurations typically involve different specimen sizes, different loading conditions, and different loading rates. For a comparison of G_{IC} and tan δ to be valid, both quantities have to be calculated at the same effective frequency. The impact event involves a wide range of frequencies. The most important frequency of a Charpy impact test is about 1000 Hz; the tan δ curve was obtained at 3.5 Hz, a factor of about several hundred less than the highest frequencies in the impact event. So the tan δ curve would have to shift to higher temperature to match the G_{IC} curve.

The principle of thermal blunting is that in impact tests, adiabatic heating would induce crack tip blunting by softening a zone of material prior to unstable propagation. The whole process is to increase the impact fracture toughness as would be measured from an effectively higher test temperature (which is equal to the sum of the test temperature and the adiabatic temperature rise). The effective temperature of the local material, T_e, in the crack tip region can be estimated by

$$T_e = T + \Delta T \tag{11}$$

where T is the test temperature and ΔT is the temperature increasing which can be calculated from

$$\Delta T = G_{IC}/(\pi\rho ckt)^{1/2} \tag{12}$$

Table II G_{IC}, t, ΔT, and T_e of PEK-C as a Function of Test Temperature

T (°C)	t (ms)	G_{IC} (kJ/m^2)	ΔT (°C)	T_e (°C)
15	4.025	3.54	5.62	20.62
40	3.950	3.84	6.16	46.16
70	4.075	4.09	6.45	76.45
100	4.025	9.36	14.87	114.87
140	3.950	5.24	8.40	148.40
180	3.875	13.85	22.42	202.42
200	3.425	3.50	6.03	206.03
240	3.575	1.66	2.80	242.80

where ρ is the density, c is the specific heat, k is the thermal conductivity, and t is the loading time. Consider PEK-C, we have ρ = 1.309 g/cm^3, c = 0.26 cal/g°C, k = 0.22 w/m°C, and t in these tests is approximately 4.0 ms. Thus, ΔT and T_e at different test temperatures can be calculated (Table II) and shown in Figure 6. From Figure 6 we can see that when the test temperature is at 100°C, T_e = 114.87°C, which is below its softening temperature. Therefore, thermal blunting becomes ineffective at 100°C. Recalling that the peak of β transition occurs at about 140°C, we may conclude that in the temperature range from 100 to 140°C, the increase in impact toughness is a result of the β transition. Normally, tan δ has a less pronounced effect on the energy absorption process than that of crack tip blunting. It is therefore expected that tan δ loss becomes operative only when the effective temperature of the local material at the crack tip is lower than the softening temperature. At 180°C, T_e = 202.43°C, which is just above the softening temperature, 200°C. Therefore, thermal blunting becomes effective at about 180°C. The enhancement in impact toughness is caused by the crack tip thermal blunting effect due to the adiabatic heating. The extent of

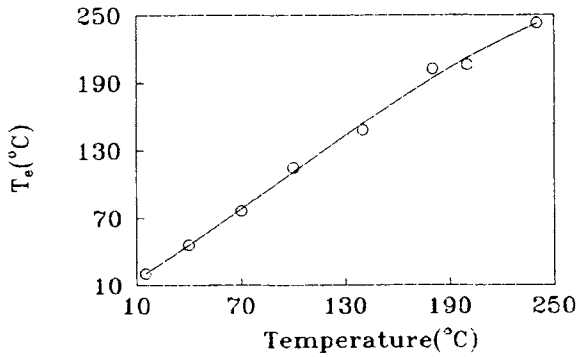


Figure 6 T_e of PEK-C vs. temperature.

the thermal crack blunting is amplified with increasing test temperature, leading to a steady increase in toughness. However, when the temperature at which PEK-C starts to lose its strength is reached, a reduction in toughness occurs and this happens at 200°C, as shown in Figure 4.

Kinloch et al.[24] have recently put forward another reason for the high fracture toughness observed for pure and rubber-modified epoxies in impact testing, namely dynamic effects instead of thermal blunting. They showed that G_{IC} is primarily determined by the time to failure (t) (which is also true for the thermal blunting mechanism) and that G_{IC} is large if t is small and the true impact fracture energy can only be obtained if t is large when dynamic effects are negligible. While dynamic effects have been shown to give high fracture toughness at short failure times because the actual energy absorption in crack initiation is overestimated, it is also obvious from the observations recorded above that crack blunting due to adiabatic heating has also occurred. Dynamic effects alone cannot explain thermal blunting in the form of stretched zones formed at the crack tip. We suspect that G_{IC} would be large under these impact testing conditions, not only due to dynamic effects, but also largely due to thermal blunting of the crack tip. However, we do agree that the high G_{IC} values in short-time impact tested specimens measured from the energy loss after impact can be due to dynamic effects and crack tip thermal blunting operating simultaneously. For PEK-C, the variation of the time to failure t at different temperatures is not very obvious, so we consider that the dynamic effects can be negligible in our discussion of temperature effect on impact fracture toughness.

From the above discussion, we can conclude that tan δ loss and crack tip thermal blunting are of particular importance when the temperature effect on impact fracture toughness is considered.

Fracture Toughness in Static and Impact Conditions

Strain rate has a significant effect on the fracture toughness of many polymers and it has been investigated extensively by Yamini and Young,[15] Kinloch et al.,[16,17] Williams and coworkers,[18,19] and Low and Mai[25] at different testing conditions. In general, the fracture toughness of polymers depends upon strain rate and temperature and there is a general equivalence between these two factors. The fracture behavior observed at low temperatures and high strain rates can be reproduced at high temperatures with low strain rates. This behavior is known as the time–temperature superposition.[26] Comparisons of the two sets of fracture toughness values obtained in the same temperature range but with two different strain rates (5 mm/min, 3.8 m/s) are given in Figure 7. The time–temperature superposition behavior is obvious. If the curve representing the impact tests is shifted to the left along the temperature axis, it is found that the results in the temperature range 15–140°C have the same trend as the static J_{IC} results in the temperature range 12–100°C. This suggests that the fracture behavior observed in impact tests at a relatively higher temperature range is similar to that obtained in the static fracture tests, but carried out in a low temperature domain.

CONCLUSIONS

PEK-C was tested under static and impact testing conditions to determine temperature effect on the fracture toughness. In the static test, when the temperature is below 100°C, LEFM is valid; when the temperature is above 100°C, LEFM is invalid and J-integral was used. In the impact test, the LEFM approach was also used.

Testing temperature markedly affects the fracture toughness of the polymer tested. The static fracture toughness increases with temperatures between 12 and 70°C as a result of the plastic blunting of the crack tip caused by the β-transition loss process of the polymer. The impact fracture toughness increases with temperature until about 100°C, which is due to the relaxation process. However, when the effective temperature at the crack tip reaches the softening temperature of the polymer due to adiabatic heating, there is a dramatic increase in fracture toughness caused by thermal blunting.

Strain rate has a strong influence on the fracture toughness of the polymer. The relationship between fracture toughness and temperature observed in the

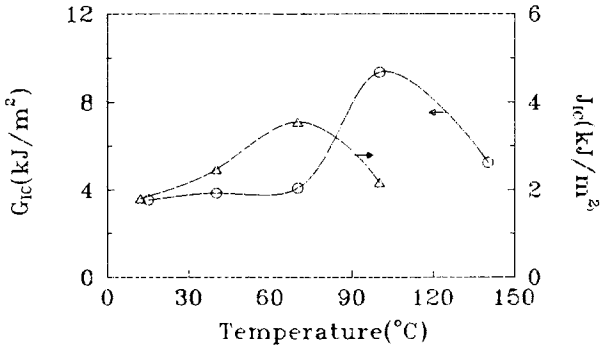


Figure 7 G_{IC} and J_{IC} of PEK-C vs. temperature.

impact tests at high temperatures is equivalent to that in the static tests at low temperatures indicating the existence of a time–temperature equivalence.

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