Mechanical Properties of Phenolphthalein Polyether Ketone: Yield Stress, Young's Modulus, and Fracture Toughness

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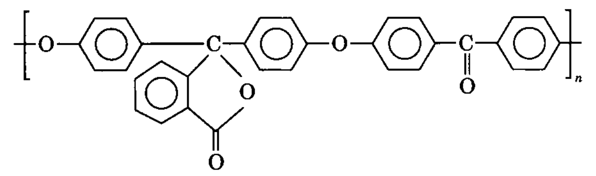
SYNOPSIS

A series of tensile and three-point bending studies was conducted at various temperatures and loading rates using phenolphthalein polyether ketone (PEK-C). Yield stress, Young's modulus, fracture toughness, and crack opening displacement data were obtained for various conditions. In general, both yield stress and Young's modulus increase with decreasing temperature. However, the relationships between fracture toughness, loading rate, and temperature are very complex. This behavior is due to the simultaneous intersection of viscoelasticity and localized plastic deformation. The increased yield stress is the main factor contributing to the reduction in fracture toughness and crack opening displacement. The relationship between fracture toughness and yield stress are discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Phenolphthalein polyether ketone (PEK-C) is a relatively new aromatic polymer. It has a glass-transition temperature (T_g) of 215°C. This implies a high temperature performance. The chemical structure of PEK-C is



PEK-C is a thermoplastic material and as such it can be converted into a range of component shapes and sizes by the full spectrum of fabrication technologies (extrusion, injection molding, etc.). PEK-C as a thermoplastic undergoes the widest conceivable range of processing methods to produce engineering components. PEK-C as a composite material provides the widest mechanical properties spectrum so far achieved by a thermoplastic. It is not surprising therefore that PEK-C has considerable potential in engineering applications, which is only just beginning to be realized. These applications can be in various areas of engineering including aerospace, automotive, bearings, and electrical. As PEK-C is being increasingly used in engineering applications there is a need to understand its mechanical properties (e.g. fracture toughness, tensile properties, etc.). This understanding also embraces the various parameters that influence these properties (e.g. temperature, strain rate, etc.).

Considerable effort has been devoted to the determination of the tensile properties and fracture toughness of many polymers. Polymeric materials, because of their viscoelasticity, are extremely sensitive to strain rate and temperature. The purpose of the present work is to study the effects of temperature and loading rate on the yield stress, Young's modulus, fracture toughness, and crack opening displacement (COD) of PEK-C. If quantitative relationships between yield stress, Young's modulus, fracture toughness, and both temperature and loading rate can be developed, they will be of use in formulating and evaluating models for fracture mechanics in PEK-C.

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EXPERIMENTAL

Materials

The material used in this work was PEK-C supplied by Xu Zhou Engineering Plastic Co. China. The molar molecular weight of PEK-C is 3.26×10^5.

Tensile Properties

Test specimens were dumbbell shaped with dimensions of $3.14 \times 3.78 \times 25$ mm. Uniaxial stress–strain relations were determined using an Instron 1121 tensile testing machine. The load and crosshead displacement were recorded on a strip chart recorder. The details of the testing procedures used are described in ASTM D638. The experiments were conducted as a function of the temperature and strain rate. Strain and strain rate were calculated from the specimen gauge length and crosshead displacement measured as a function of time. Several tensile properties, such as yield stress and Young's modulus were calculated based on the load-displacement curves.

Fracture Toughness

Fracture mechanics characterization was performed in three-point bending with a span-to-width ratio of 4, using an Instron 1121 tensile testing machine, at different temperatures, at a constant crosshead speed of 5 mm/min, and at room temperature at different crosshead speeds. Specimens were single-edge notched $80 \times 16 \times 8$ mm bars. Sharp notches were introduced by scalpel-sliding a razor blade having a one edge tip radius of 13 μm.

For materials that exhibited brittle behavior, the critical stress intensity factor, K_{IC}, at fracture initiation was determined according to ASTM Standard E399-83 for metals.[1] The values of K_{IC} are given by:

$$K_{IC} = Y(a/W)\sigma_c a^{1/2} \tag{1}$$

where $Y(a/W)$ is a geometrical correction factor, σ_c is the gross applied stress, and a is the initial crack length. For a single-edge notched bend specimen (SENB) with $S/W = 4$, the geometrical correction factor is given by:

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

K_{IC} is related to the energy per unit area of the fracture G_{IC} by the relationship

$$K_{IC}^2 = EG_{IC}/(1 - \nu^2) \tag{3}$$

where E is the elastic modulus, ν is Poisson's ratio.

For the characterization of fracture toughness in more ductile materials, the J-resistance curve, J_R, according to the multispecimen technique covered by ASTM Standard E813-81[2] was used. Each of several specimens were loaded to a different deflection, and J was calculated from the input energy U, measured at the final deflection according to the expression

$$J = 2U/B(W - a) \tag{4}$$

where B, W, and a are the specimen thickness, width, and initial notch length, respectively. The specimens tested were then fractured completely at a higher speed to change the fracture regime and, therefore, the fracture surface morphology. The initial crack growth length and the amount of crack extension could thus be measured from the surface of completely broken samples with a microscope.

The J values obtained are then plotted against the measured Δa, giving the J_R curve. Because with ductile materials some crack tip blunting may occur prior to the real crack propagation, to determine the onset of crack extension according to ASTM E813-81,[2] the J vs. Δa curve is extrapolated to intersect the blunting line, assumed to be expressed by:

$$J = 2\Delta a\sigma_y \tag{5}$$

where σ_y is the tensile yield stress, the intersection gives the fracture resistance, J_{IC}, at fracture initiation, and the slope $dJ/d\Delta a$ of the linear region of the J_R curve represents the resistance to crack propagation.

In all the fracture tests performed, the size requirement set by standards E399-83 and E813-81 for the validity of both K_{IC} and J_{IC}, respectively, were always met.

RESULTS AND DISCUSSION

Yield Stress

The temperature and the strain rate dependence of yield stress of PEK-C are shown in Figures 1 and 2, respectively. Yield stress decreases with increasing temperature and decreasing strain rate.

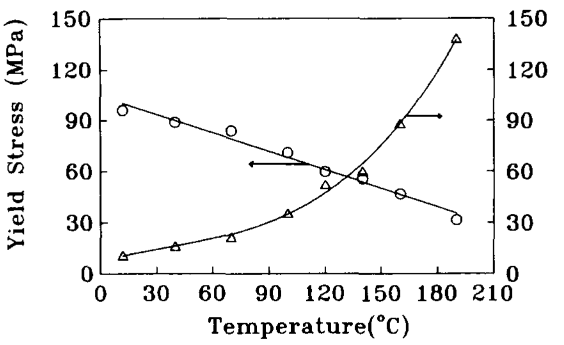

Figure 1 Yield stress, σ_y and COD, δ_o vs. temperature.

The temperature and the strain rate dependence of the yield behavior of polymers have been modeled using the Eyring theory of viscosity.[3,4] For temperatures below the glass-transition temperature, but above the secondary or the β transition temperature of the polymer, the expression for the yield stress is

$$\frac{|\sigma_y|}{T} = \frac{R}{V^*}\sin h^{-1}\left[\frac{\dot{e}}{2A_E}\exp\left(\frac{\Delta E^*}{RT}\right)\right] \qquad (6)$$

where σ_y is the yield stress, $\dot{e}$ is the strain rate, and A_E is a material constant. At the high stresses typically encountered at the yield in glassy polymers, eq. (6) can be approximated, assuming $\sin h(x) = \exp(x)/2$ (i.e. for large x) as:

$$\frac{|\sigma_y|}{T} = \frac{\Delta E^*}{V^*T} + \frac{R}{V^*}\ln\left(\frac{\dot{e}}{A_E}\right) \qquad (7)$$

ΔE^* in the above equation is a measure of the activation energy, that is the energy required by the segments of the polymer backbone chain under the influence of the yield stress and thermal energy to jump from one equilibrium position to another, and V^* is the volume of a polymer segment involved in the yield stress.

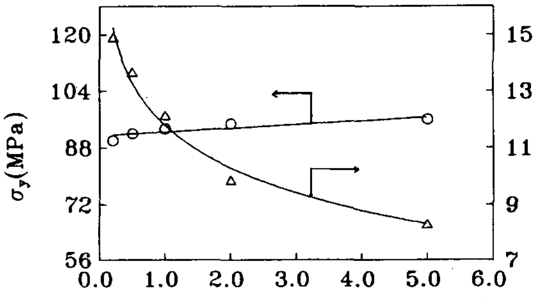

Figure 2 Yield stress, σ_y and COD, δ_o vs. crosshead speed at room temperature.

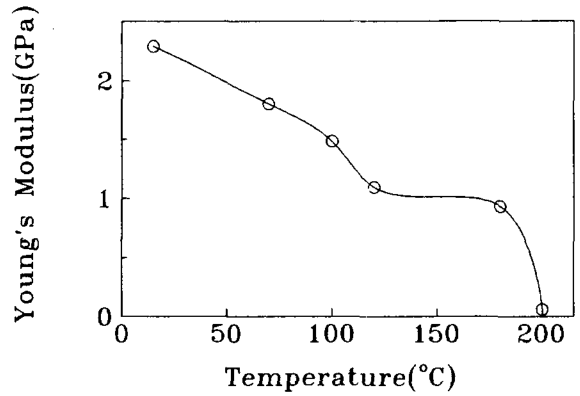

Figure 3 Young's modulus of PEK-C as function of temperature.

For a given material, that is constant A_E, and for tests conducted at constant strain rates, the Eyring model predicts a linear relationship between yield stress and temperature. The results in Figure 1 confirm the linear behavior for PEK-C of this study.

Young's Modulus

The temperature and the strain rate dependence of Young's modulus are shown in Figures 3 and 4, respectively. Young's modulus increased with increasing strain rate and decreasing temperature.

Relationship Between Yield Stress and Young's Modulus

From the above results, we can see that any variable that increases Young's modulus also increases yield stress. The theories to look at the relationship between Young's modulus and yield stress over a wide range of temperatures were derived by Bowden et

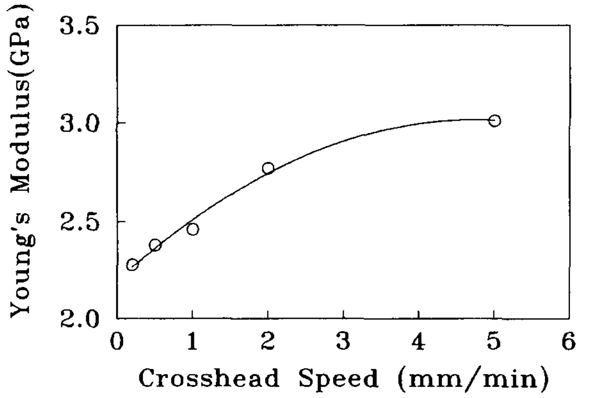

Figure 4 Crosshead speed dependence of Young's modulus.

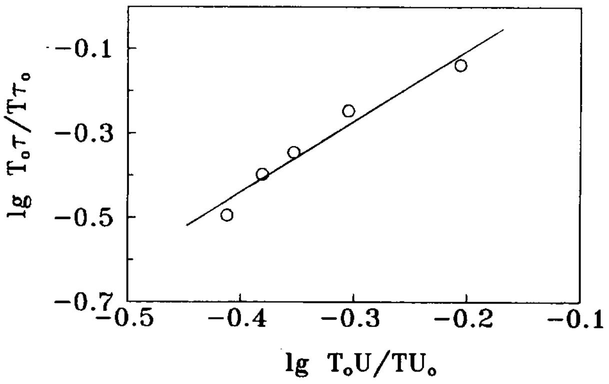

Figure 5 Relationship between τ and U.

al.[5-7] and Argon et al.[8-10] Kitagawa[11] has recently expanded and generalized Bowden's theory showing that the relationship between U and τ can be represented by a power law relation of the form

$$\frac{T_o\tau}{T\tau_o} = \left(\frac{T_oU}{TU_o}\right)^n \tag{8}$$

where τ_0 and U_0 are the values of shear yield stress and shear modulus at some reference temperature T_0 (conveniently taken as the ambient temperature), and n is a temperature independent exponent.

To test the applicability of this theory, it is necessary to convert the moduli and yield stresses into the corresponding shear moduli and shear yield stresses. This can be done using the equations:

$$U(T) = E(T)/2(1 + \nu) \tag{9}$$

$$\tau(T) = \sigma_y(T)/\sqrt{3} = 3^{1/2} \tag{10}$$

Kitagawa showed that a relation of the form of eq. (8) held over a wide range of temperatures for most polymers. He also found that the exponent had

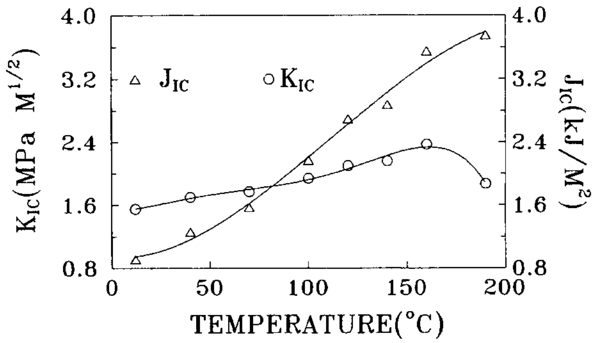

Figure 6 Temperature dependence of fracture toughness.

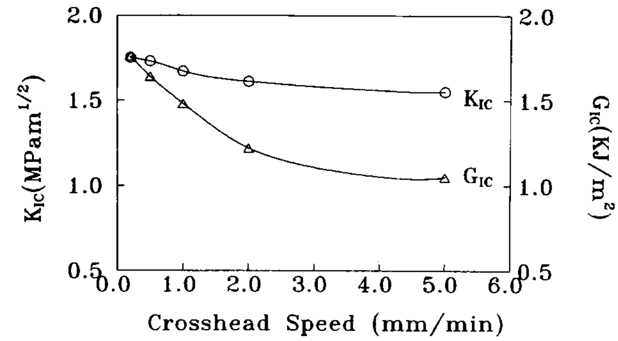

Figure 7 K_{IC} and G_{IC} of PEK-C as a function of crosshead speed.

a unique value of 1.63 for all amorphous polymers, and between 0.8 and 0.9 for semicrystalline polymers. Figure 5 is a log–log plot according to eq. (8) for the values of τ and U obtained for PEK-C tested over a wide range of temperatures. The line drawn on the graph has a slope of 1.67 and it can be seen that all points fall close to this line. All these results show that yield stress and Young's modulus are correlated over a wide range of temperatures.

Fracture Toughness

The results of fracture mechanics tests are shown in Figures 6 and 7, respectively. At room temperature, at the crosshead speed over the range from 0.2–5 mm/min and at constant crosshead speed from room temperature to 70°C, the material exhibited brittle fracture behavior, and gives valid linear elastic fracture mechanics (LEFM) data, so we use K_{IC} to describe its fracture behavior. G_{IC} can be obtained with eq. (3). With increasing temperatures from 100 to 190°C, the material becomes more ductile and LEFM was invalid. Another method J-integral was used. The value of J

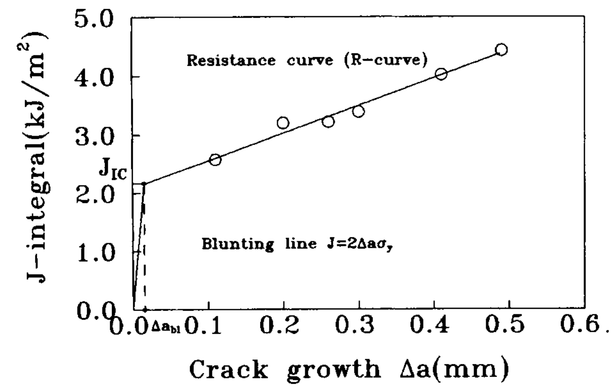

Figure 8 Schematic J-integral-crack extension, Δa curve at 100°C.

for each specimen was calculated using eq. (4). Figure 8 shows the results at 100°C plotted on a single graph as J vs. Δa. Also shown in the same figure is the blunting line based on eq. (4) and the least square fitted line to the crack extension points. J_{IC} is determined at the intersection of these two lines. The values of J_{IC} at other temperatures are also obtained by the same method. The equivalent values of K_{IC} were given by the relation

$$K_{IC}^2 = EJ_{IC}/(1 - \nu^2) \tag{11}$$

where E is the Young's modulus.

As shown in Figure 6, J_{IC} increases with increasing temperature, K_{IC} increased with increasing temperature up to near T_g, peaked at about T_g, and then dropped off with further increasing temperature.

The relation between decreased fracture toughness and increased crosshead speed has been discussed. As shown in Figure 7, both K_{IC} and G_{IC} of PEK-C exhibited negative dependence on strain rate, that is, $dK_{IC}/\dot{e} < 0$ and $dG_{IC}/\dot{e} < 0$.

In general, the fracture toughness of polymers depends upon temperature and strain rate and there is general equivalence between these two factors. The fracture behavior observed at low temperatures and high strain rates can be reproduced at higher temperatures with slow strain rates. This behavior is known as the time–temperature superposition.[12]

COD

Various models such as those of Irwin[13] and Dugdale[14] have been proposed to describe the extent and shape of the localized plastic deformation zone at a crack tip. From these models one may define a parameter known as the COD. δ_o and the value of δ_o for the onset of crack growth is given by

$$\delta_o = K_{IC}^2/E\sigma_y \tag{12}$$

where K_{IC} is the stress intensity factor at the onset of crack growth, σ_y is the tensile yield stress, and E is Young's modulus. Values of the crack opening displacement at the onset of crack growth are shown as a function of test temperature and test rate for PEK-C in Figures 1 and 2, respectively. The values of δ_o increase with increasing temperature and decreasing rate.

Relationship Between Fracture Toughness and Yield Stress

During fracture initiation dissipative mechanisms are prevalent and associated with the formation of a zone of plastic deformation, which is in turn controlled by the yield behavior at the crack tip.

In an attempt to formulate the K_{IC} and σ_y relationship, the following argument is proposed. Considering a crack propagation at a crack velocity $\dot{a}$, the strain rate of the crack tip, $\dot{e}_{\text{tip}}$, for the moving crack is derived by Williams[15] based on viscoelastic analysis, namely

$$\dot{e}_{\text{tip}} = \pi(E/K_{IC})^2 e_y^3 \dot{a} \tag{13}$$

where E is Young's modulus and e_y is the yield strain.

Furthermore, the relationships of K_{IC} against $\dot{a}$ and σ_y against the strain rate $\dot{e}$ are customarily expressed by[16]

$$K_{IC} = A\dot{a}^n \tag{14}$$

and

$$\sigma_y = B + C \log \dot{e} \tag{15}$$

where A, B, C, and n are constants. Equation (15) is in fact a specific form of eq. (7), for the case of constant T.

At the crack tip, eq. (15) becomes

$$\sigma_y = B + C \log \dot{e}_{\text{tip}} \tag{16}$$

Substituting eq. (14) into (13) we obtain

$$\dot{e}_{\text{tip}} = \pi E^2 e_y^3 K_{IC}^{(1/n)-2}/A^{1/n} \tag{17}$$

Combining eqs. (16) and (17) gives

$$\sigma_y = \alpha + \beta \log K_{IC} \tag{18}$$

or

$$\log K_{IC} = (\sigma_y - \alpha)/\beta \tag{19}$$

provided that

$$\alpha = B + C \log(\pi E^2 e_y^3/A^{1/n}) \tag{20}$$

and

$$\beta = C(1/n - 2) \tag{21}$$

Equations (3) and (19) can be combined to give

$$\log G_{IC} = 2\sigma_y/\beta - (2\alpha/\beta + \log E) + \log(1 - \nu^2) \tag{22}$$

Figure 9 illustrates the relationships between log K_{IC}, log G_{IC}, and σ_y for PEK-C, which exhibit linear relationships.

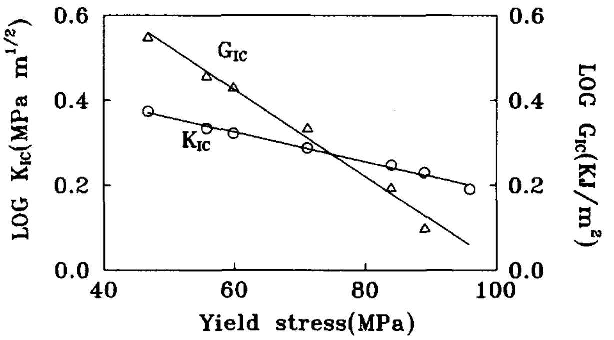

Figure 9 K_{IC} and G_{IC} vs. yield stress.

For J_{IC} and yield stress, it is already established[17,18] that

$$J_{IC} = \delta_o \sigma_y \tag{23}$$

both δ_o and σ_y are temperature/test rate-dependent.[19] If the decrease in yield stress outweighs the increase in COD, the fracture toughness is reduced with temperature increase (or test rate decrease). If the increase in COD outweighs the decrease in yield stress, the fracture toughness increases with temperature increase (or test rate decrease). Obviously, the decrease in yield stress with increasing temperature (or decreasing test rate) satisfactorily explains the increasing fracture toughness for PEK-C.

From the above results, we concluded that the yield behavior at the crack tip is the main factor controlling the plastic deformation and thus the fracture toughness. In other words, considering the relationships between the yield stress and temperature/strain rate, and the fracture toughness and the yield stress, it is obvious that a decrease in fracture toughness is related to the increased yield stress of the materials.

CONCLUSIONS

A series of tensile and three-point bending measurements was made on PEK-C at various temperatures and loading rates. Based on these measurements, the following conclusions were reached:

1. Yield stress is a linear function of temperature and log strain rate. The temperature and the strain rate dependence of the yield stress can be modeled by the Eyring theory.
2. Young's modulus increases with decreasing temperature and increasing strain rate. The relationships between yield stress, Young's modulus, and temperature is obtained.
3. Fracture toughness and COD are all increased with increasing temperature and decreasing strain rate. The relationships between fracture toughness, loading rate, and temperature is very complex. This behavior is due to the simultaneous intersection of viscoelasticity and localized plastic deformation. The increased yield stress is the main factor contributing to the reduction in fracture toughness and COD. The relationships between fracture toughness, COD, and yield stress are obtained.

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