Relationship Between Viscoelastic Transition and Yield Behavior of Phenolphthalein Poly(ether ketone)

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SYNOPSIS

The viscoelastic behavior of phenolphthalein poly(ether ketone) (PEK-C) and its relationship to yielding was studied. The following phenomena were observed: (1) The relaxation behavior at strain near yield closely approximated that at low strain but near the T_g; (2) the temperature and strain rate dependence of yield stress could be modeled by the one-process Eyring theory and the value of the activation volume was the same as that of the glass transition; and (3) according to the Zhurkov–Bueche equation, the α transition was related to the yield behavior. All these results indicated that the glass transition was the main factor that controlled the yield behavior. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A considerable effort has been devoted to the determination of the viscoelastic and yield behavior of many polymers. Polymeric materials, because of their viscoelasticity, are extremely sensitive to strain rate and temperature. The analysis of these properties of polymers can be very different from that of metals because of the apparent viscoelastic effects.

To date, the analysis of polymer yield behavior has mostly involved the evaluation of macroscopic phenomena. Less attention has been paid to the development of an understanding at the molecular level. In present study, we discuss the viscoelastic behavior and its relationship to the yielding of phenolphthalein poly(ether ketone) (PEK-C).

PEK-C is a relatively new aromatic polymer with a high glass transition temperature, which implies its possibility of being a high-temperature-performance polymeric material. It can be used as an engineering thermoplastic and a matrix of composites. Because PEK-C is being increasingly used in engineering applications, there is a need to understand its viscoelastic and yield properties.
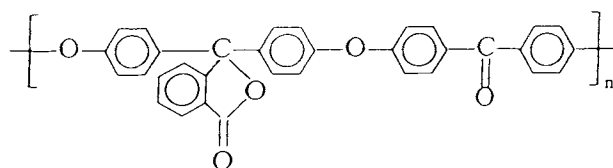
EXPERIMENTAL

Material

The material used in this study was phenolphthalein poly(ether ketone) (PEK-C) supplied by the Xu Zhou Engineering Plastic Co., China, according to the patent technology of the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in the form of powder (its reduced viscosity in chloroform at a temperature of 25°C is 0.49 dL/g). 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 the required specimens on a JSW-17SA injection-molding machine (Japan) with barrel temperatures of 325–360°C. The pellets were also compression-molded into the required specimens (thin film about 0.2 mm in thickness) at 310°C and 45 MPa.

Relaxation Measurement

Dynamic Properties

The dynamic properties of the sample were measured on a Rheovibron Model DDV-II-EA. The compression-molded sample (3.71 cm in length, 0.43 cm in width, and 0.021 cm in thickness) was heated at a rate of 2°C/min over the range from room temperature to 250°C. The frequency used was 3.5 Hz.

Stress-Relaxation Test

Stress-relaxation measurements were carried out at different temperatures on an Instron tester (Model 1121). All the series of measurements were performed starting from the highest measuring temperature. Before each measurement, the sample specimen was heated 10 min to reach the thermal equilibrium. In an effort to minimize physical aging at higher temperatures, the specimens were kept at room temperature for as long as possible, rapidly heated to the test temperature, and tested as soon as thermal equilibrium was reached. To ascertain that we were in the linear viscoelastic range, we chose the strain as 1%. The crosshead speed was 20 mm/min. The modulus was calculated according to eq. (1):

$$E(t) = P(t)/A_0\varepsilon \qquad (1)$$

where $E(t)$ is the modulus; $P(t)$, the load; A_0, the original cross-sectional area; and ε, the strain.

Uniaxial Tensile Test

Test specimens were injection-molded dumbbell-shaped with dimensions of $3.14 \times 3.78 \times 25$ (mm)^3. Uniaxial stress–strain relations were determined using an Instron 1121 tensile testing machine from room temperature to near the glass transition temperature. Some measurements were also made at the strain rates from 0.002 to 2 min^{-1} at room temperature. The details of the testing procedures used were described in ASTM D638. The load and crosshead displacement were recorded on a strip chart recorder. Strain and strain rates were calculated from the specimen gauge length and crosshead displacement measured as a function of time. Five replicates were run at each temperature and strain rate, and all five specimens were put into the oven simultaneously. The mean values of yield stress were calculated based on the load-displacement curves.

RESULTS AND DISCUSSION

Mechanical Relaxation

Dynamic Properties

Figure 1 shows the results of the storage modulus (E'), loss modulus (E''), and tan δ of PEK-C obtained from Rheovibron DDV-II-EA as a function of temperature at 3.5 Hz. From the results, we can see that there was a small increase in E'' around 143.8°C, similar to that seen in the tan δ curve. On the other hand, there was a slight decrease in E'. These suggested a secondary transition at a somewhat low temperature. Due to its position and intensity, it was associated with a β process and probably was related to a restricted motion of the main chain of the polymer (crankshaft mechanism).[1] With the temperature increasing, one can observe a larger peak around 241.7°C in the tan δ and E'' curves along with a regular decrease in E'. These changes were due to the glass transition of the sample.

Stress Relaxation

The relaxation moduli $E(t)$ were obtained at a strain level of 1% at eight different temperatures for PEK-C. A different specimen was used for each run. The temperature ranged from 20 to 190°C; eight sets of the results of PEK-C are shown in Figure 2, where the relaxation modulus $E(t)$ was plotted against time on a linear-log graph. According to the principle of time–temperature equivalence,[2] the master curves of PEK-C at an arbitrary reference temperature were obtained by shifting along the time axis. The plot of shift factors and master curves are shown in Figures 3 and 4, respectively.

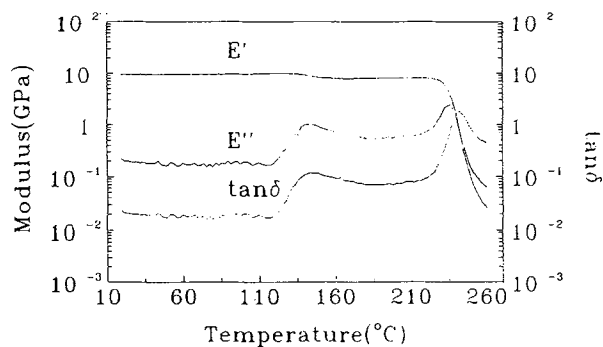We can apply the coupling model[3–5] to describe the stress-relaxation behavior of PEK-C:

Figure 1 The elastic modulus (E'), loss modulus (E''), and tan δ of PEK-C as a function of temperature at 3.5 Hz.
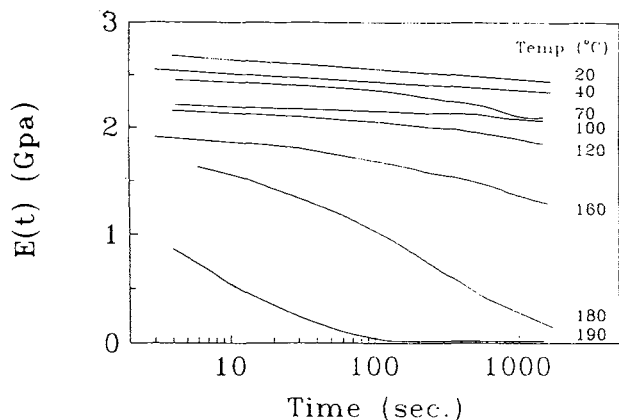
Figure 2 Tensile stress-relaxation modulus of PEK-C as a function of logarithm time at different temperatures.

Figure 4 Master curves of PEK-C at different reference temperatures.

$$E(t) = Er + \Delta E \exp - (t/\tau_p)^{1-n} \qquad (2)$$

$$\tau_p = [(1 - n)w_c^n \tau_0]^{1/(1-n)} \qquad (3)$$

where Er is the relaxed modulus; ΔE, the relaxation strength; n, the coupling parameter; and τ_p, the effective relaxation time.

n is the most important parameter in the coupling model, since it is characteristic of the breadth of relaxation. According to the coupling model, it represents microscopically the strength of coupling between a relaxing species and its surroundings. The temperature dependence of n of PEK-C is shown in Figure 5. n decreases with increasing temperature; before reaching the glass transition, the change is very small, but when approximately reaching the glass transition, n decreases obviously.

We also carried out the stress-relaxation test at a strain level of yield strain at room temperature. The parameter n obtained at yield strain was smaller than that obtained at a strain of 1%. This means
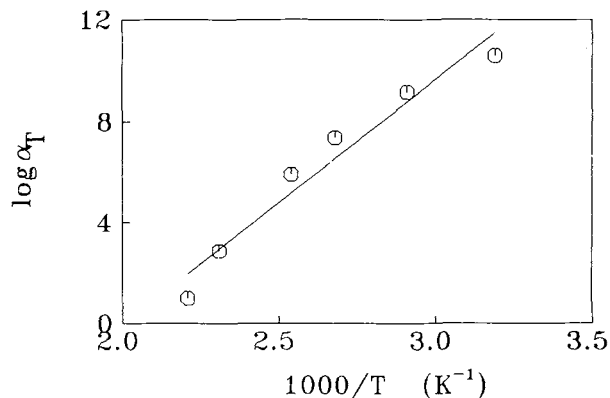
that the strains also have the effect of changing the parameter n. In terms of the coupling model, this means that the relaxing species is becoming less and less coupled to its surroundings. Put another way, elevated strain induces a more liquidlike structure in the material. The value of n obtained at the T_g is equal to that obtained at yield strain. This indicates that at a strain near yield the material can actually relax as if it were at the T_g (although the actual temperature remains constant) and flow becomes possible.

The above experimental results clearly demonstrate the ability of both temperature and strain to significantly alter the relaxation behavior of glassy PEK-C. Approaching either the yield strain or glass transition temperature produces nearly the same relaxation behavior. This implies that the elevated strain at incipient yield induces a structure in the polymer that relaxes in a manner comparable to that of the polymer near its T_g.

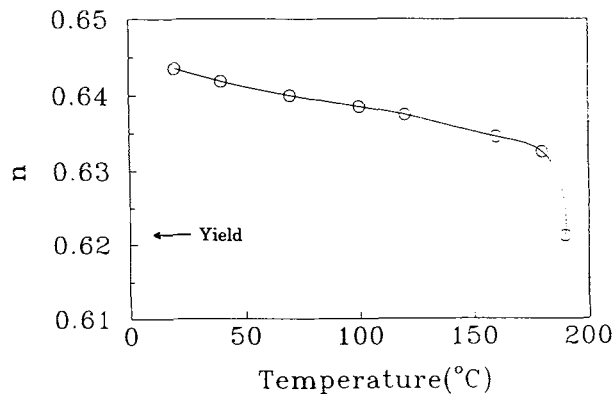**Figure 3** Logarithmic shift factors of PEK-C as a function of inverse temperature.

Figure 5 The coupling parameter n of PEK-C as a function of temperature.

Yield Stress

Figures 6 and 7 show the yield stress as a function of temperature and log strain rate, respectively. The yield stress decreased with increasing temperature and decreasing log strain rate. The temperature and the strain-rate dependence of the yield behavior of polymers were modeled using the Eyring theory of viscosity.[6-8] For high values of stress, it can be expressed by eq. (4):

$$\sigma_y = \Delta H/V + (kT/V)\ln(2\dot{\varepsilon}/\dot{\varepsilon}_0) \qquad (4)$$

For a given material and for tests conducted at a constant strain rate, the Eyring model predicts a linear relationship between yield stress and temperature. The results in Figure 6 confirmed the linear relationship for PEK-C of this study. Equation (4) indicates that the plot of σ_y/T vs. log $\dot{\varepsilon}$ gives a linear relationship (Fig. 7). Values of ΔH and V can be obtained from the slope and the intercept of Figures 7 and 6; they are 60.9 kcal/mol and 0.9 nm³, respectively.

From the stress-relaxation data, we can also evaluate the activation volume V.[9,10] When the stress is plotted against the logarithm of time, the maximum slope of the curve, F, defined as $[-d\sigma(t)/d \ln t]_{max}$, can be expressed as eq. (5) according to the theory of the stress-dependent thermal activation (SDTA) concept applied on the stress relaxation[11]:

$$F = [-d\sigma(t)/d \ln t]_{max} = kT/V \qquad (5)$$

Thus, we can calculate the value of V from the stress-relaxation measurement, which is 0.93 nm³. It is the same as that obtained from the yield behavior. This indicates that the flow units are the same when the stress-relaxation and yield behavior occur.
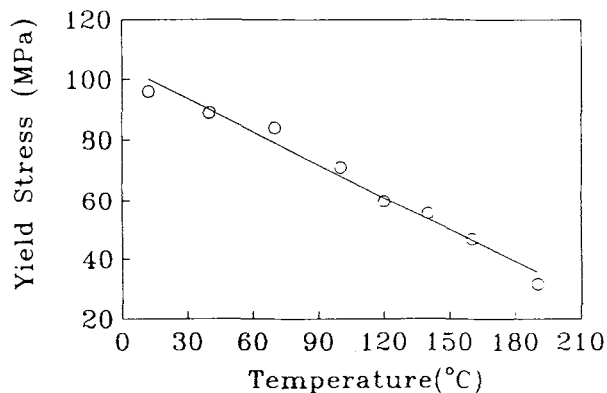

Figure 6 Yield stress of PEK-C as a function of temperature.
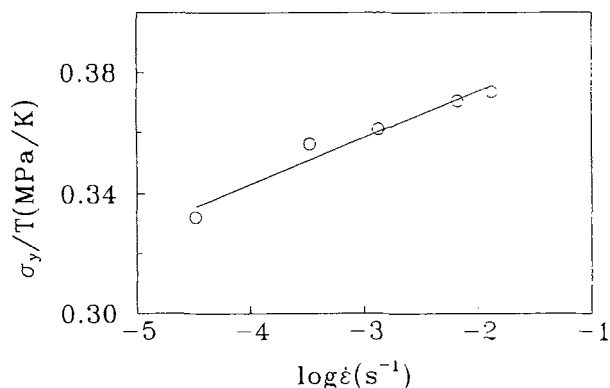

Figure 7 Ratio of yield stress to temperature as a function of the logarithm of the strain rate of PEK-C.

Another explanation for which viscoelastic mechanism plays an important role in the uniaxial tensile failure mechanism can be based on the Zhurkov–Bueche equation[12] wherein the apparent E_a represents the difference between the E_a for a major process and the work applied [the product of a stress, σ, and the activation volume V; eq. (6)]:

$$E_a(\text{apparent}) = E_a(\text{molecular process}) - \sigma V \qquad (6)$$

The activation volume in eq. (6) should be the activation volume for the process being considered. The apparent activation energy for the tensile strength measurement is 60.9 kcal/mol; the tensile strength of 100 MPa is used in eq. (6) to determine the activation volume.

When the β transition is considered, the activation energy of the governing process is 31.6 kcal/mol; substituting E_a = 31.6 kcal/mol into eq. (6), the activation volume is calculated to be less than zero. It has no physical meaning.

On the other hand, when the glass transition is considered, the activation energy of the governing process is 61.2 kcal/mol. For the apparent activation energy of 60.9 kcal/mol, the activation volume is found to be 0.79 nm³, which is similar to the result obtained by the Eyring equation.

From above results, we can conclude that, for uncracked specimens in a tensile test, the values of activation energy and activation volume suggest that the glass transition process is important in governing the molecular processing involving the yielding.

CONCLUSIONS

The viscoelastic behavior of phenolphthalein poly-(ether ketone) (PEK-C) and its relationship to yield-

ing was studied. The following results were obtained:

1. The relaxation behavior at strain near yield closely approximated that at low strain but near the T_g.
2. The temperature and strain-rate dependence of the yield stress could be modeled by the one-process Eyring theory and the value activation volume was the same as that of the glass transition.
3. According to the Zhurkov–Bueche equation, the α transition was related to the yield behavior.

All these results indicated that the glass transition was the main factor that controlled the yield behavior.

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