

# Viscoelastic Properties of Phenolphthalein Poly(ether ketone)\*

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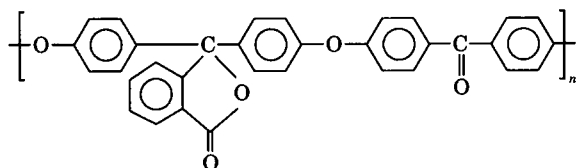
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## SYNOPSIS

Stress relaxation and dynamic mechanical behavior of phenolphthalein poly(ether ketone) (PEK-C) have been investigated. Using Ferry's reduction method, the master curve was obtained. From the experimental results, we found that the WLF equation is not appropriate in the lower-temperature range ( $T < T_g$ ). The relaxation spectrum was calculated according to the first approximation method proposed by Schwarzl and Staverman. In addition to the  $\alpha$ -transition region, a second transition zone is revealed at low temperature. This transition is probably due to a restricted motion of its main chain. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Phenolphthalein poly(ether ketone) (PEK-C) is a relatively new aromatic polymer with a high glass transition temperature ( $T_g$ ). This implies a high-temperature performance. The chemical structure of PEK-C is



PEK-C is of great interest at the present time because it can be used in a variety of applications for which common plastics are inadequate due to their low resistance to temperature. As we continue to use PEK-C in structural components, it is essential to consider the time-temperature-dependent performance of it. From our knowledge of viscoelasticity, we can take the conventional stress re-

laxation and dynamic mechanical effect into design consideration.

## EXPERIMENTAL

The material used in this study was phenolphthalein poly(ether ketone) (PEK-C) supplied by Xu Zhou Engineering Plastic Co., China, according to the patent technology of 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 0.47 dL/g). The original powders were dried at 120°C for 1 day to remove moisture 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 made into thin film about 0.2 mm in thickness at 310°C, 45 MPa. Later, the film was cut into 30 mm (L) × 4 mm (W) dumbbell test specimens for stress relaxation.

Relaxation measurements were carried out at different temperatures on an Instron tester (table Model 1121). All series of measurements were performed starting from the highest measuring temperature. Before each measurement, the sample specimen was heated 10 min in order to reach the thermal equilibrium. To ascertain that we were in

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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):

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

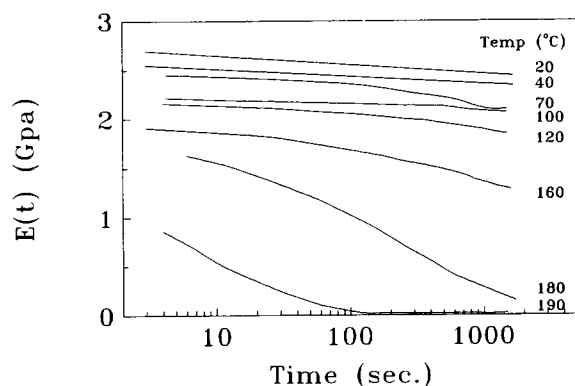
where  $E(t)$  is the modulus;  $P(t)$ , the load;  $A_0$ , the original cross-sectional area; and  $\varepsilon$ , the strain.

The dynamic properties of the samples were measured on a Rheovibron Model DDV-II-EA. The samples were heated at a rate of 2°C/min over the range from room temperature to 250°C. The frequency used was 3.5 Hz.

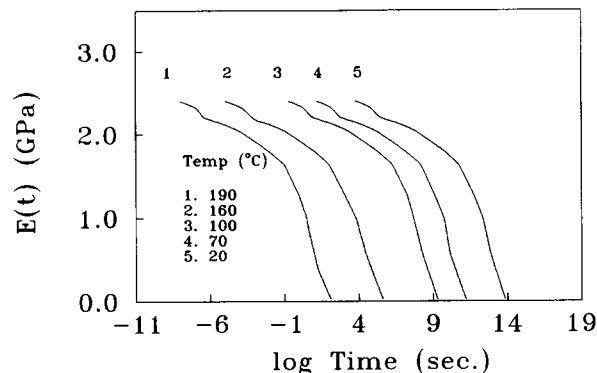
## RESULTS AND DISCUSSION

### Stress-relaxation Data

Typical data of the stress relaxation of PEK-C at different temperatures ranging from room temperature to 190°C are shown in Figure 1, where the relaxation modulus  $E(t)$  is plotted against time on a linear-log graph. Using Ferry's reduction method, all the results were reduced to an arbitrary temperature,  $T_0$ . We neglected a correction for thermal expansion and for temperature variation of the elastic modulus due to rubber elasticity. We assumed  $T_0\rho_0/T\rho$  to be unity.  $\rho_0$  and  $\rho$  are the densities of the sample at temperatures  $T_0$  and  $T$ , respectively. Thus, we composed the smooth master curve of stress relaxation as shown in Figure 2 for PEK-C. All the relaxation curves were satisfactorily superposed by sliding them along the time axis using only an experimental shift factor,  $\alpha_T$ , at each temperature. Only a few points deviate from the master curve,



**Figure 1** Tensile stress-relaxation curves of PEK-C as a function of temperature.



**Figure 2** Master curves of PEK-C at different reference temperatures.

and these deviations are believed to be due to experimental scatter.

In Figure 1, there is an abrupt hump in the 70°C data near 900 s. This shows up on the master curves (Fig. 2) as the abrupt modulus drops in the range of 2.2–2.5 GPa, which are independent of temperature and time. This is ascribed to the  $\beta$ -transition. At intermediate times, the decrease in the modulus is due to the glass transition.

### Shift Factor and Apparent Activation Energy

The temperature dependence of the shift factor is expected to obey the well-known WLF equation:

$$\log \alpha_T = -C_1(T - T_0)/(C_2 + T - T_0) \quad (2)$$

Equation (2) can be rewritten in the form

$$-(T - T_0)/\log \alpha_T = (T - T_0)/C_1 + C_2/C_1 \quad (3)$$

where  $\alpha_T$  is the shift factor at temperature  $T$ ;  $T_0$ , the reference temperature; and  $C_1$  and  $C_2$ , constants. They were determined by using the classical graphical method suggested by Ferry.<sup>1</sup> For this purpose,  $-(T - T_0)/\log \alpha_T$  was plotted against  $T - T_0$ , and from slope  $s$  and intercept  $i$  of the resulting straight line, the empirical constants were calculated:

$$C_1 = -1/s \quad (4)$$

$$C_2 = i/s \quad (5)$$

The molecular meaning of the coefficients  $C_1$  and  $C_2$  can be more precise by the assumption of some concepts from free-volume models, namely: (1) viscosity depends on the free volume according to the well-

known Doolittle equation and (2) the fractional free-volume  $f$  increases with temperature according to the equation

$$f = f_g + \alpha_f(T - T_0) \quad (6)$$

where  $\alpha_f$  is the thermal expansion coefficient of the free volume above  $T_g$ , and  $f_g$ , the fractional free volume at  $T_g$ . Thus, the following relation holds:

$$C_1 = B/2.3f \quad (7)$$

$$C_2 = f/\alpha_f \quad (8)$$

where  $B$ , an empirical constant in the Doolittle equation, is usually assumed to be unity. Equations (7) and (8) yield values of  $f/B$  and  $\alpha_f/B$ , if  $C_1$  and  $C_2$  are available.

From our experimental data (Fig. 3), we obtained  $C_1 = 4.08$  and  $C_2 = -74.24$ . Since  $C_2 < 0$ , according to eq. (8), it has no physical meaning. This indicates that the WLF equation is inappropriate below  $T_g$ .

The deviation from the WLF equation in the lower-temperature range seems to be a common feature for all polymers. It was previously noted for other amorphous and crystalline polymers.<sup>2,3</sup> As was pointed out by Ferry et al. when studying the polymethacrylate series, the relaxation process in the glassy zone is due to thermal motion of the side chain or of localized small portions in the main chain, whereas the relaxation process in the transition region is due to the micro-Brownian movement of the molecule or to short-range cooperative segmental diffusion. So, it is understandable that the experimental shift factor  $\log \alpha_T$  diverges from the WLF equation which applies in a temperature zone ranging from  $T_g$  to  $T_g + 100$  where the micro-Brownian movement of the molecule or a short-range cooperative segmental diffusion process prevails.

Similar considerations account for the deviation from the WLF equation in the higher-temperature range. The relaxation process in the plateau region differs from that in the transition region. It is postulated that the relaxation process in the plateau zone is an intermolecular process due to the loosening of entanglements, whereas the process in the transition zone is an intramolecular process. It is reasonable to think that the validity of the WLF equation is doubtful in the plateau region even if a smooth master curve is obtained by shifting relaxation curves along the time axis.

The above argument results in having agreement

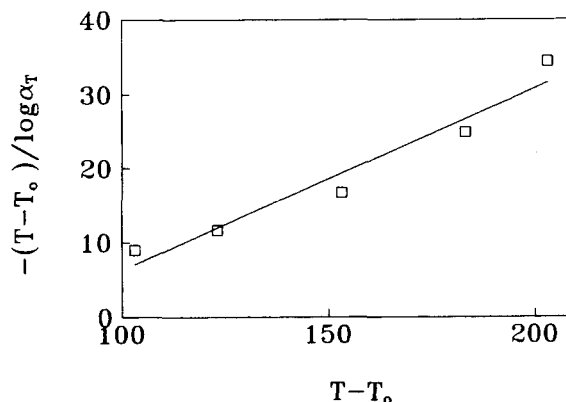


Figure 3  $-(T - T_0)/\log \alpha_T$  vs.  $T - T_0$  at reference temperature of 190°C.

between the WLF equation and the experimental shift factor in a range between  $T_g$  and  $T_g + 100$  for linear amorphous polymers. The presence of branching, crosslinking, or crystallinity considerably narrows this region.

It is also possible that the deviation of  $\log \alpha_T$  from the WLF prediction is a consequence of the correction factor  $f(t)$  which was not applied below  $T_g$ . In fact, no appropriate theory permits one to make this correction in the glassy state. In several instances, it is not important. But when the modulus-time dependence is as slight as it is in Figure 1 at temperature lower than  $T_g$ , the correction may become important and influence significantly the shift factors determined.

By treating the relaxation process as a chemical reaction, an apparent activation energy  $\Delta H$ , which measures the stiffness of the chain against the segments' motion, can be calculated from the data of the shift factor using the well-known equation

$$\Delta H = 2.303Rd(\log \alpha_T)/d(1/T) \quad (9)$$

where  $R$  is the gas constant and the factor  $d(\log \alpha_T)/d(1/T)$  is obtained from the slope of Figure 4. The value of  $\Delta H$  calculated for PEK-C is 61.2 kcal/mol.

### Distribution of Relaxation Times

The distribution of relaxation times  $H(\tau)$  or the relaxation spectrum of PEK-C was obtained from its master curve using the first method of approximation proposed by Schwarzl and Staverman<sup>4</sup>:

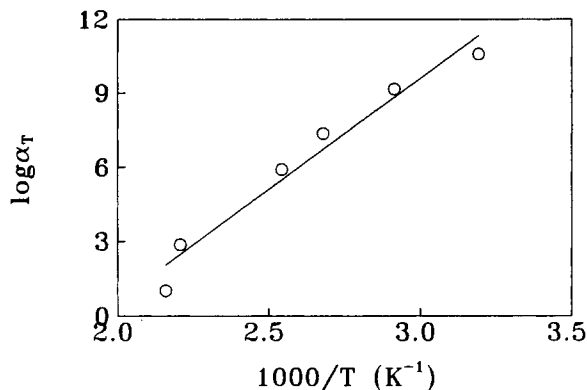


Figure 4  $\log \alpha_\tau$  of PEK-C vs.  $1/T$ .

$$H(\tau) = -dE(t)/d \ln t|_{t=\tau} \quad (10)$$

The spectrum is shown in Figure 5 on a log-log graph. The spectrum has a peak which is due to the  $\alpha$ -transition.

#### Observed Dynamic Data

To confirm the stress-relaxation analysis of the PEK-C sample, dynamic mechanical properties were measured on a Rheovibron DDV-II apparatus, at 3.5 Hz, as a function of temperature. The experimental values of  $\tan \delta$  were presented in Figure 6. One observes a large peak around 241.7°C which is obviously related based on our stress-relaxation measurements to the  $T_g$  of the sample. It is expected to have a higher  $T_g$  by the dynamic method as compared to the one obtained by the static method (stress relaxation) since different frequencies were used in the two sets of experiments. One can also observe part of a small peak,

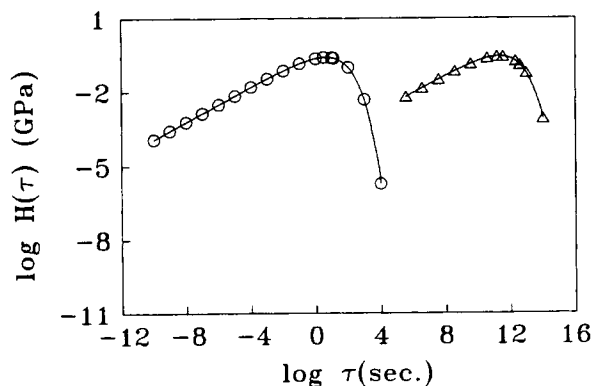


Figure 5 Stress-relaxation spectrum of PEK-C at different reference temperatures: (OOO) 190°C; ( $\Delta\Delta\Delta$ ) 20°C.

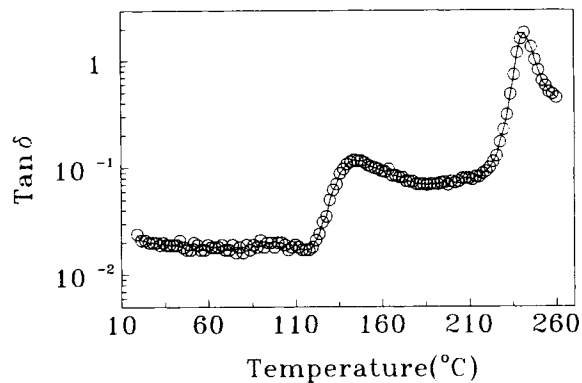


Figure 6 Temperature dependence of  $\tan \delta$  of PEK-C at 3.5 Hz.

around 143.8°C, associated with a secondary relaxation of the polymer.

In Figure 7, the values of  $E'$  and  $E''$  of PEK-C, as obtained experimentally at 3.5 Hz, are plotted against temperature. A small increase in  $E''$  around 143.8°C is observed, similar to that seen in the  $\tan \delta$  curve (Fig. 6). Above 241.7°C, a maximum in  $E''$  along with a regular decrease in  $E'$  are observed. Both changes are due to the glass transition of the sample.

From dynamic measurements, a small rise in intensity has been observed at 143.8°C, suggesting a peak at a somewhat low temperature. Due to its position and intensity, this peak is probably associated with a  $\beta$  process. It is probably associated with a restricted motion of the main chain of the polymer (crankshaft mechanism).<sup>5</sup> Further studies at higher frequencies are necessary to elucidate this point.

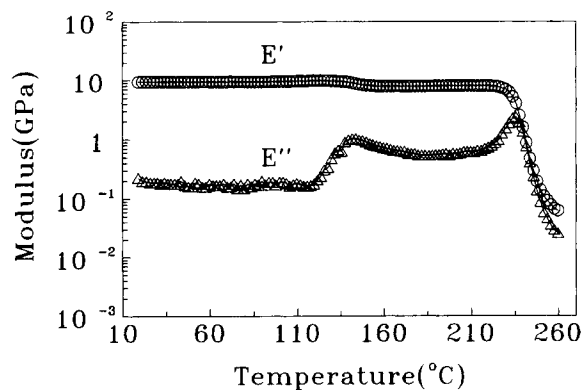


Figure 7 Elastic and loss moduli of PEK-C as a function of temperature at 3.5 Hz.

## CONCLUSIONS

Stress relaxation and dynamic mechanical behavior of phenolphthalein poly(ether ketone) (PEK-C) have been investigated over a wide range of temperature. Using Ferry's reduction method, the master curve was obtained. From the master curve, the relaxation time spectrum, shift factor, and apparent activation energy was calculated. The temperature dependence of shift factor indicated that the WLF equation was inappropriate below  $T_g$ . From the results of the measurements, we found that PEK-C had a  $\beta$ -transition around 143.8°C, which maybe is due to a restricted motion of its main chain.

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