Polymer Vol. 37 No. 14, pp. 2975–2979, 1996

0032-3861/96/$15.00+0.00

Application of coupling model for stress relaxation of phenolphthalein polyether ketone*

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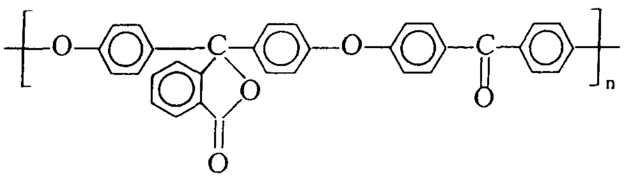
(Received 29 June 1995; revised 22 November 1995)

According to stress relaxation curves of phenolphthalein polyether ketone (PEK-C) at different temperatures and the principle of the time–temperature equivalence, the master curve of PEK-C at arbitrary reference temperature is obtained. A coupling model is applied to explain quantitatively stress relaxation behaviour of PEK-C at different temperatures. The parameters obtained from the coupling model have important physical meaning. Copyright © 1996 Elsevier Science Ltd.

(Keywords: phenolphthalein polyether ketone (PEK-C); stress relaxation; time–temperature equivalence)

INTRODUCTION

Phenolphthalein polyether ketone (PEK-C) is a relatively new aromatic polymer. It has a glass transition temperature (T_g) of 200°C. The molecular weight is 2.3×10^5. 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 moulding, 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 applications including aerospace, automotive industry, etc., where common plastics are inadequate due to their low resistance to temperature. As PEK-C is being increasingly used in engineering applications there is a need to understand its mechanical properties. Because of their viscoelasticity, mechanical properties of polymeric materials are different from those of metals. In order to characterize the mechanical properties of PEK-C properly and understand the viscoelastic contribution more quantitatively, not only for application but also for theoretical analysis, it is very important to study its stress relaxation behaviour at different temperatures.

Stress relaxation has been investigated widely[1,2]. According to stress relaxation curves at different temperatures and the principle of time–temperature equivalence, the master curve at an arbitrary reference temperature can be obtained, and we can also obtain important parameters which describe stress relaxation behaviour such as shift factor and relaxation time as a function of temperature.

There are many models[3] to describe the stress relaxation phenomenon, such as WLF (Williams, Laudel and Ferry) and the Arrhenius equation. But the WLF equation is usually suitable for the temperature between T_g and $T_g + 100$°C. The reason we apply the coupling model[4–6] to explain the stress relaxation phenomenon is that the model can describe not only stress relaxation but also dielectric relaxation, volume recovery and dynamic light scattering, etc.[7–9]. From this model we can obtain some important parameters, such as effective relaxation time and coupling parameter, which have some relationship with its mechanical properties. Thus, we can establish relationships between different properties through the coupling model and from viscoelastic viewpoint to interpret the mechanical properties. These we will discuss in a separate paper.

Coupling model of relaxation

The coupling model[10–18] of relaxation addresses the following question: What is the effect of coupling a single primitive relaxation mode to a 'complex' system? Consider a single relaxation mode in a polymer, for instance the α relaxation. By 'coupling' to this mode, we mean the effects of molecular cooperativity and other interactions with its complex environment in the bulk

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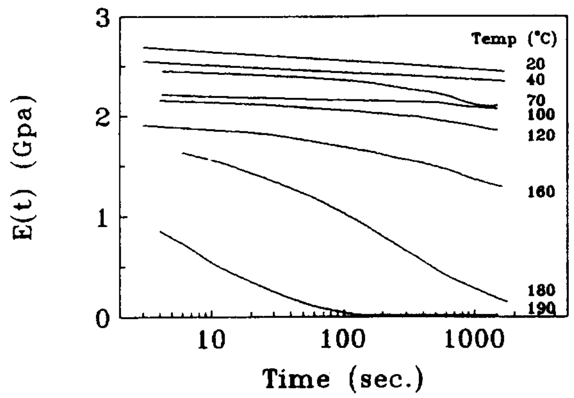

Figure 1 Tensile stress relaxation curves of PEK-C, as a function of time at different temperatures

polymer. A glassy polymer is a particular example of a complex system, but the coupling model has been found to be applicable to a more general range of systems. All of these complex systems lack long-range spatial order but have sufficient residual short-range order that identical fundamental relaxation species can be defined throughout the material. Motions of the fundamental mode on small spatial scales are well-defined, but as the relaxations develop, they encounter cooperativity and complexity. This results in a slowing down of the process.

At sufficiently short times before molecular cooperativity sets in, coupling of the primitive relaxation mode to its complex environment need not be considered, and the relaxation rate τ_0^{-1} is independent of time and the same for each relaxing species. This will be the situation for times less than a time $t_c \equiv \omega_c^{-1}$ that is characteristic of the cooperative response of the complex environment. The relaxation quantity $Q(t)$ then obeys a simple rate equation with a constant relaxation rate

$$\frac{dQ(t)}{dt} = -\tau_0^{-1}Q(t) \qquad \omega_c t \ll 1 \tag{1}$$

This leads to a simple exponential decay of $Q(t)$ from the initial unrelaxed value Q_u towards the relaxed value of Q_R. If we write the solution of equation (1) as $Q(t) = (Q_u - Q_R)\phi(t) + Q_R$, then

$$\phi(t) = \exp(-t/\tau_0) \qquad \omega_c t \ll 1 \tag{2}$$

The relaxation time for the primitive relaxation mode is τ_0. At times longer than t_c, the relaxation of the primitive mode must involve sequential, cooperative or tandem adjustment, and response of its complex environment and hence is slowed down. The results of this coupling to complexity can be quantitively described in terms of a diminished relaxation rate. The constant relaxation rate τ_0^{-1} which described the process in the absence of coupling effects if reduced by a time-dependent factor of the form $(\omega_c t)^{-n}$, $0 < n < 1$. The relaxing quantity then obeys:

$$\frac{dQ(t)}{dt} = -\tau_0^{-1}(\omega_c t)^{-n}Q(t) \qquad \omega_c t \gg 1 \tag{3}$$

The rate becomes modified by a time-dependent factor, and this reflects the slow adjustments of the complexity on spatial scales larger than the short range order.

If the relaxation rate is modified as in equation (3), this leads to a slower than exponential decay of the form:

$$\phi(t) = \exp\left[-\int_0^t dt'\tau_0^{-1}(\omega_c t)^{-n}\right] \qquad \omega_c t \gg 1 \tag{4}$$

if the material-dependent rate parameters τ_0, n, and ω_c are constant on the timescale of the relaxation experiment. Examples of this situation are during linear response experiments or if the material structure is unchanged. In this case, equation (4) integrates to a simple exponential of a fractional power of time or 'fractional exponential'

$$\phi(t) = \exp\{-t^{1-n}/[(1-\mathrm{n})\omega_c^n \tau_0]\} \tag{5}$$

$$\phi(t) = \exp[-(t/\tau_p)^{1-n}] \tag{6}$$

$$\tau_p \equiv [(1-n)\omega_c^n \tau_0]^{1/1-n} \tag{7}$$

Here the effective relaxation time τ_0 of the complex system has been defined, and it is predicted to be related to the relaxation time τ_0 of the primitive relaxation mode by equation (7). Equations (6) and (7) are both predictions of the coupling model, and they both involve the same parameter n. Therefore, if the value n were determined, by fitting fractional exponential into equation (7) one can predict the relation between τ_p and τ_0.

EXPERIMENTAL

The material used for this programme was PEK-C supplied by Xu Zhou Engineering Plastic Co. 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^{-1}).

The original powders were dried at 120°C for 1 day to remove moisture, and then 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, 40 MPa. Later the film was cut into 30 mm $(L) \times 4$ mm (W) dumb-bell test specimens for stress relaxation.

Stress 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 for 10 min in order to reach thermal equilibrium. We chose a strain of 1% in order to work near the linear region. The crosshead speed is 20 mm min^{-1}. The modulus was calculated according to the following formula:

$$E(t) = P(t)/A_0\epsilon \tag{8}$$

where $E(t)$ = modulus at t; $P(t)$ = load at t; A_0 = cross-sectional area; ϵ = strain.

RESULTS AND DISCUSSION

Typical data of stress relaxation of PEK-C at different temperatures ranging from 20°C to 109°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 could be reduced to

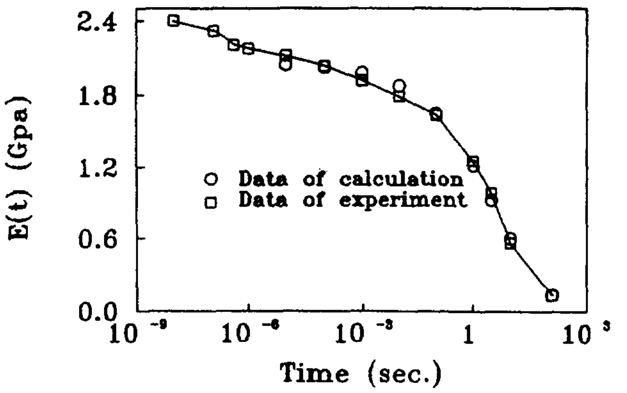

Figure 2 Master curve of PEK-C at reference temperature 190°C

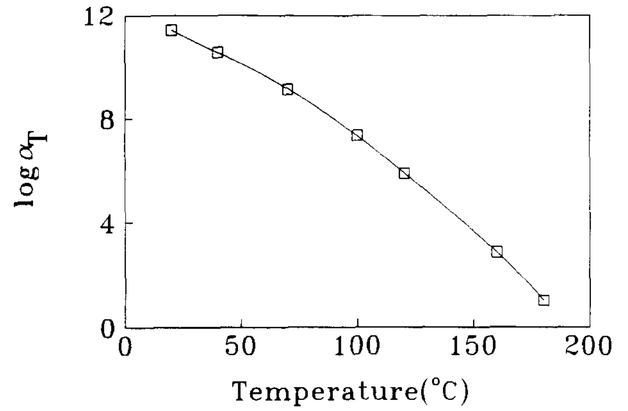

Figure 3 Temperature dependence of shift factor of PEK-C at reference temperature 190°C

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. ρ_0 and ρ are the densities of the sample at temperatures T_0 and T, respectively. Thus we composed the smooth master curve of stress relaxation of PEK-C at a reference temperature of 190°C (*Figure 2*). All the relaxation curves are satisfactorily superposed by sliding them along the time axis using an experimental shift factor, a_T, at each temperature (the temperature dependence of the shift factor, a_T, is shown in *Figure 3*). Only a few points deviate from the master curve, and these deviations are believed to be due to experimental scatter.

As shown in *Figures 1* and *2* PEK-C has two transitions, α transition and β transition, in experimental range. Here we mainly explain α transition using a coupling model.

Applying the coupling model to the time-dependent modulus $E(t)$ gives:

$$\frac{\mathrm{d}E(t)}{\mathrm{d}t} = -\omega_0(\omega_c t)^{-n}E(t) \tag{9}$$

In general, all three parameters ω_0, ω_c and n are functions of the material structure, and are therefore expected to change with external conditions such as temperature, physical aging, deformation, etc. However, if the material structure is assured to remain constant, then equation (9) can be integrated. The results can be written as a pair of equations:

$$E(t) = E_r + \Delta E \exp\left[-(t/\tau_p)^{1-n}\right] \tag{10}$$

$$\tau_p \equiv [(1-n)\omega_c^n \tau_0]^{1/1-n} \tag{7}$$

where E_r is the relaxed modulus, ΔE is the relaxation strength, n is the coupling parameter in the coupling model, and τ_p is effective relaxation time.

According to equation (10), we compiled a computer program, and used stress relaxation data at different temperatures to calculate parameters E_r, ΔE, τ_p and n at different temperatures (*Table 1*). From the calculation, ΔE and E_r are constant at different temperatures, E_r being about 0.02 GPa, and ΔE being about 2.65 GPa. Calculation results and experimental data were consistent.

The temperature-dependence of n of PEK-C is shown in *Figure 4*. n will decrease as temperature increases. Before reaching T_g, the change is very small, but when approximately reaching T_g, n decreases obviously. Because n changes with temperature, by the time–temperature equivalence, n will also change with relaxation time at a fixed temperature.

The temperature-dependence of τ_p is shown in *Figure 5*. τ_p drastically decreases with increasing temperature. When reaching T_g, τ_p is very small, the temperature-dependence of τ_p changes at 100°C, which is due to the existence of β transition. Effective relaxation time, τ_p, from calculation, and the relaxation time τ from experiment are consistent (*Table 1*).

If the master curve by shifting along the time axis is compared with the curve obtained from the coupling model, we find the two curves are the same (*Figure 2*). On the other hand the value of E_r, ΔE and τ_p from calculation is consistent with from experiment. All these illustrate that the coupling model is reasonable. We can use this model to describe the stress relaxation phenomenon.

In the coupling model, τ_0, n, and ω_c have a physical interpretation. The actual values of the rate parameters τ_0, n, and ω_c are quite dependent on the material structure and the relaxation process under consideration.

As mentioned before, ω_c is a frequency that characterizes

Table 1 The dependence of E_r, ΔE, τ_p, τ and n on temperature

T(°C)	190	180	160	120	100	70	40	20
E_r (GPa)	0.02	0.03	0.02	0.03	0.02	0.04	0.01	0.02
ΔE (GPa)	2.58	2.63	2.53	2.64	2.65	2.63	2.66	2.65
n	0.621	0.632	0.635	0.638	0.639	0.640	0.642	0.644
τ (s)	3.10	1.70×10^2	7.00×10^3	2.00×10^6	7.00×10^7	5.50×10^9	1.50×10^{11}	2.50×10^{12}
τ_p (s)	4.67	2.53×10^2	5.65×10^3	2.84×10^6	1.08×10^8	7.79×10^9	2.17×10^{11}	3.60×10^{12}

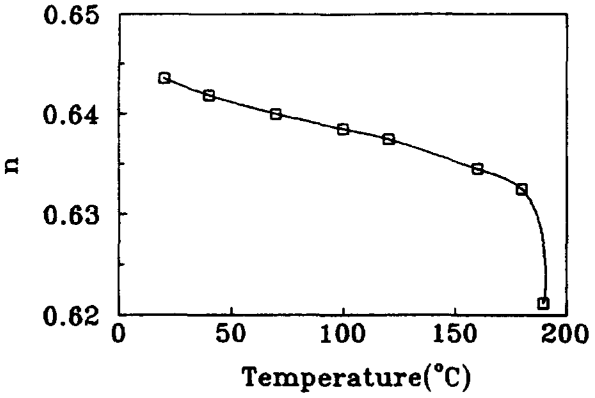

Figure 4 The coupling parameter *n* of PEK-C as a function of temperature

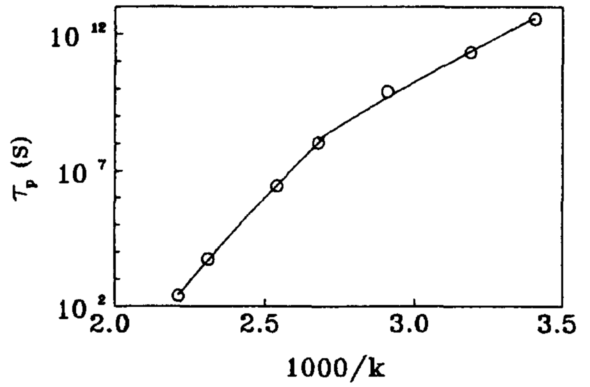

Figure 5 The effective relaxation time of PEK-C as a function of temperature

the complexity of the system, and for polymers it typically lies in the neighbourhood of 10^9–10^{10}s^{-1}. The values of ω_c can be independently determined in many cases using another property of equations (6) and (7), which is called crossover. The regime where $\omega_c\tau_0 \gg 1$ (e.g. low temperatures) is dominated by a fractional exponential. The crossover from exponential to fractional exponential occurs near $\omega_c T_0 \simeq 1$. This crossover phenomenon can be examined in polymers using dynamic light scattering data. These additional crossover predictions of the coupling model have been verified and they allow the value of ω_c to be determined.

n is the coupling parameter in the coupling model, and is perhaps the most important, 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. *n* varies from 1 to 0. An *n* of 1 indicates a high degree of coupling (a perfectly elastic solid). An *n* of 0 would describe a completely uncoupled system (isolated molecule) and the factor $(\omega_c t)^{-n} \simeq 1$ so that there is little modification of the rates and the rates are nearly independent on time. For stronger coupling, *n* takes larger values leading to slow relaxation rates.

As far as we know, no other model has produced the prediction between τ_p and τ_0. τ_0 is the relaxation time of the underlying primitive mode. The coupling model leads to the predictions between τ_p and τ_0. Equation (7) can be used to predict how the fundamental relaxation time τ_0 and its dependence on physical variables is modified by coupling to give rise to the effective relaxation time τ_p for the bulk system. Suppose it were known from measurements that the relaxation time for the primitive relaxation mode had certain dependences on temperature (T), pressure (P), stress (σ), and other physical variables: $\tau_0 = \tau_0(T,\ P,\ \sigma,\ M,\ \ldots\ \ldots)$. Then equation (7) would predict modified dependences for the relaxation time τ_p:

$$\tau_p(T,P,\sigma,M,\ldots\ldots)\ \alpha\ [\tau_0(T,P,\sigma,M,\ldots\ldots)]^{1/1-n} \qquad (11)$$

For example, suppose it were known that τ_0 had a simple Arrhenius temperature dependence:

$$\tau_0(T) = \tau_\infty \exp\,(E_a/RT) \qquad (12)$$

Then inserting this into equation (7), $\tau_p(T)$ would be predicted to have a modified temperature dependence:

$$\tau_p(T) = [(1-n)\omega_c^n\tau_\infty]^{1/1-n}\exp[Ea/(1-n)RT]$$
$$\equiv \tau_{p\infty}\exp[E_a^*/RT] \qquad (13)$$

where

$$\tau_{p\infty} \equiv [(1-n)\omega_c^n\tau_\infty]^{1/1-n} \qquad (14)$$

$$E_a^* \equiv E_a/(1-n) \qquad (15)$$

Measurements on the bulk polymer would be predicted to find $\tau_p(T)$ described by a modified prefactor $\tau_{p\infty}$ and a modified effective activation barrier E_a^*, which is related to the true molecular activation barrier E_a of the fundamental model. E_a^* and E_a are related by the factor $1/(1-n)$ where *n* is the coupling strength parameter. Since $0 < n < 1$ then $E_a^* > E_a$, which reflects the cooperativity required for motions in a bulk polymer. These predictions can be tested by comparing to actual measurements. The remarkable thing is that these predictions and others resulting from equations (6) and (7) are quantitatively verified in case after case.

The coupling model predicts the effects of coupling and cooperativity on the motions of a single relaxation mode. In some situations there may be contributions from different primitive relaxation modes. For instance, in viscoelasticity there can be contributions from secondary as well as primary relaxations. In this situation, each relaxation mode would be subjected to modification by the coupling mechanism. The coupling of different modes to the complex environment is generally different giving rise to different *n* values for each mode.

The coupling mechanism is a more quantitative and refined concept for dealing with cooperativity than concepts used previously such as free volume. There is no contradiction between the coupling mechanism and free volume whenever the latter is applicable; however, the coupling mechanism is more generally applicable. The coupling model is also not restricted to polymer systems. This is advantageous for viscoelasticity because stress relaxation measurements on silicate glasses, metallic glasses and other systems show many similarities to polymer results.

CONCLUSIONS

According to stress relaxation curves of phenolphthalein polyether ketone (PEK-C) at different temperatures and the principle of time–temperature equivalence, the master curve at arbitrary reference temperature is obtained. We use the coupling model to describe the stress relaxation phenomenon, the data of calculation and the data of experiment are consistent. This shows the coupling model is fitted to describe the stress relaxation of PEK-C.

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