

SHORT COMMUNICATIONS

**Enthalpy Relaxation in Poly(aryl ether ketone bearing phthalidylidene group)**

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In general, glassy polymers exist in a non-equilibrium state, and tend to approach equilibrium through physical aging or annealing below its glass transition temperature  $T_g$ . During this process, the mechanical properties and thermodynamic functions would change.<sup>1-5</sup> In the past several years, there have been great interests in revealing the molecular mechanism and effect of physical aging by enthalpy relaxation in the region of glass transition using differential scanning calorimetry (DSC).<sup>6-11</sup> The kinetics of the enthalpy relaxation can be described in terms of the enthalpy lost  $\Delta H(t_a, T_a)$  due to aging when the polymer has aged for time  $t_a$  at temperature  $T_a$ . The values of  $\Delta H(t_a, T_a)$  are obtained from experimental data and follow an empirical equation proposed by Cowie *et al.*<sup>10</sup>:

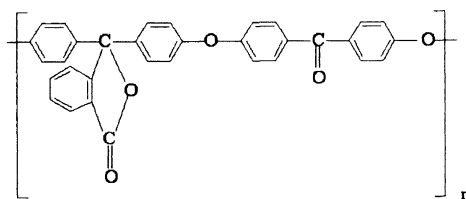
$$\Delta H(t_a, T_a) = \Delta H(\infty, T_a)[1 - \phi(t_a)] \quad (1)$$

with  $\phi(t_a) = \exp[-(t_a/t_c)^\beta]$

where  $t_c$  is a characteristic aging time,  $\beta$  a measure of the breadth of the relaxation times distribution,  $\Delta H(\infty, T_a)$  the enthalpy lost on infinite aging at  $T_a$ , and  $\phi(t_a)$  the so-called Williams-Watts relaxation function.<sup>12</sup> One of the advantages of eq 1 consists obviously in the fact that the aging behavior of a glassy polymer can be estimated easily.

As a new member of poly(ether ketone)

family, poly(aryl ether ketone bearing phthalidylidene group) (PEK-C, systematic name: poly(phthalidylidene-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)) exhibits properties at room temperature similar to those of poly(ether ether ketone) (PEEK), but is amorphous, as well as of higher  $T_g$  ( $T_g = 220^\circ\text{C}$ ), better solubility in certain solvents and more economical in cost<sup>15,16</sup>:



PEK-C has been identified as an excellent engineering thermoplastic matrix resin of high performance composites, and has great potential as separation membrane owing to the large phthalidylidene groups in the main chain.<sup>16,17</sup> The aim of the present paper is to investigate the enthalpy relaxation characteristics of PEK-C and provide knowledge for a deeper understanding of the blends with PEK-C. In addition, we suggest an approach to the evaluation of polymeric enthalpy relaxation kinetics.

## EXPERIMENTAL

In order to coincide with the sample preparation employed in our subsequent research on the blends comprised of PEK-C, solution casting was used: powdered PEK-C with a reduced viscosity of  $1.10 \text{ ml g}^{-1}$  supplied by the Xuzhou Engineering Plastics Co. of China was dissolved in 1,2-dichloroethane to make a 5% solution. And then, the solution was poured onto a clean glass plate, allowing evaporation of the solvent at room temperature. The filmy sample was removed from the glass plate and dried in vacuum at  $110^\circ\text{C}$  for 48 h.

Heat capacity  $C_p(T)$  vs. temperature  $T$  measurements were carried out on 20 mg sample with a Perkin-Elmer DSC-2C differential scanning calorimeter. According to the treatment used by Berens *et al.*,<sup>5</sup> the experimental steps were as follows. The sample was annealed at  $280^\circ\text{C}$  for 10 min, and then cooled at  $40^\circ\text{C min}^{-1}$  to  $210^\circ\text{C}$  ( $=T_a$ ) and aged for  $t_a$  min. After that, the sample was cooled to  $100^\circ\text{C}$  again at  $40^\circ\text{C min}^{-1}$ , and a heating scan was followed and recorded at  $20^\circ\text{C min}^{-1}$  to  $280^\circ\text{C}$ . The enthalpy lost  $\Delta H(t_a, T_a)$  was obtained from:

$$\Delta H(t_a, T_a) = \int_{T_1}^{T_2} [C_p(T)_{\text{aged}} - C_p(T)_{\text{unaged}}] dT \quad (2)$$

where  $T_1$  and  $T_2$  were the temperature limits selected properly, and the trace of  $C_p(T)_{\text{unaged}}$  was collected by using  $t_a = 0$  min.

## RESULTS AND DISCUSSIONS

The measured  $\Delta H(t_a, 210^\circ\text{C})$  is plotted as a function of  $t_a$ , as shown in Figure 1. By making use of the non-linear least square curve fitting procedure to eq 1, the three parameters are obtained:  $\Delta H(\infty, 210^\circ\text{C}) = 2.55 \pm 0.01 \text{ J g}^{-1}$ ,  $t_c = 52.99 \pm 0.08 \text{ min}$ ,  $\beta = 0.546 \pm 0.005$ .

The higher value of  $t_c$  might result from the

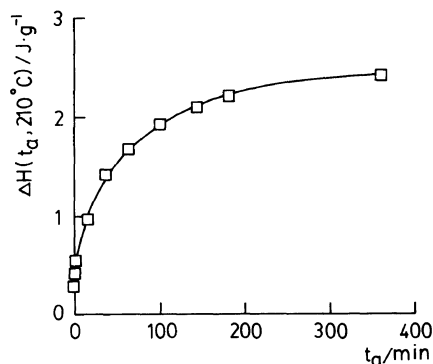


Figure 1. Enthalpy lost in PEK-C at  $210^\circ\text{C}$   $\Delta H(t_a, 210^\circ\text{C})$  vs. aging time  $t_a$ .

great steric hindrance of the bulky phthalidyldiene side groups to the limited intermolecular rotation of the main chain, which is considered the cause for the enthalpy relaxation.<sup>9</sup> And the  $\beta$  parameter is also higher, corresponding to a narrower distribution of relaxation times. This indicates that the amorphous features of PEK-C lie in the lack of ordered regions to a great extent. Because in case there are ordered regions in the polymer, the difference in mobility between the chains near and far from the immobile ordered regions will lead to a broader distribution of relaxation times.

On the other hand, a larger value of  $\beta$  is customarily regarded as a smaller value for the time taken for the enthalpy to relax to within 99.9% of the equilibrium value.<sup>11,14</sup> This is a intuitive judgment, but might lead to ambiguous data analysis, for example, in the case of higher values of both  $\beta$  and  $t_c$ , especially if one wants to compare aging behavior of various polymers. Suppose there are two kinds of polymers: polymer I and polymer II, and  $\beta_I < \beta_{II}$ ,  $t_{c,I} < t_{c,II}$  (where the subscripts "I" and "II" stand for polymers I and II, respectively, similarly hereinafter), it is factually hard to decide the difference between their kinetics of the approach to the equilibrium state in accordance with the above-mentioned criterion. So a more precise criterion which can simply compare the enthalpy relaxation

kinetics is required. From eq 1, a critical parameter  $\alpha$  is derived and given below

$$\alpha = 1 - \exp \left[ - \left( \frac{t_{c,II}}{t_{c,I}} \right)^{(\beta_I \beta_{II} / \beta_{II} - \beta_I)} \right] \quad (3)$$

On the basis of eq 3, the following deduction can be made easily: when  $\Delta H(t_a, T_a)_I / \Delta H(\infty, T_a)_I = \Delta H(t_a, T_a)_{II} / \Delta H(\infty, T_a)_{II} <$  or  $> \alpha$ , the enthalpy relaxation approaching to equilibrium in polymer I is faster or slower than that in polymer II. It seems to imply that in the earlier stage of aging,  $t_c$  governs the rate of enthalpy relaxation and  $\beta$  becomes dominant in the later stage. The analysis of the relation between  $\beta$ ,  $t_c$  and the rate of enthalpy relaxation can help to explore the details of the molecular mechanism concerned and the effect of plasticization, reinforcement, blending, etc. on polymers, and will be adopted in our further investigation on the blends with PEK-C.

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