Physical Aging of Bisphenol A Polycarbonate

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ABSTRACT: The physical aging of bisphenol A polycarbonate was studied using the differential scanning calorimetry technique. Cowie and Ferguson's model and Williams-Watts function were used to analyze the data. It is confirmed that the relation $\Delta H_\infty(T_a) = \Delta C_p(T_g - T_a)$, where $\Delta H_\infty(T_a)$ is the value of the aging enthalpy for $t = \infty$, T_a the aging temperature, and ΔC_p the difference in the specific heat above and below the glass transition temperature (T_g), can be used to study quantitatively the physical aging of bisphenol A polycarbonate. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1646–1648, 1999

Key words: physical aging; polycarbonate

INTRODUCTION

Bisphenol A polycarbonate (PC) is an engineering material of major importance because of its clarity, toughness, and dimensional and thermal stability.[1,2] When PC is heated below the glass transition temperature (T_g) and is kept at this temperature for a certain period of time, it undergoes physical aging.[1,3–5] This aging is manifested by an increase in deflection temperature, flexural and tensile strength, and a decrease in elongation at break and fracture toughness. Also, as observed from differential scanning calorimetry (DSC) measurements,[5–7] PC aged below T_g shows an endothermic peak on later heating above T_g. The precise physical origin of this behavior is not fully understood. However, it is consistent with a general phenomenon where the presence of a reasonable amount of amorphous content in any polymer shows annealing peaks.[8,9] These peaks have also been observed in poly(ether ether ketone) (PEEK),[9] poly(ethylene terephthalate) (PET), and poly(hidroxy butirate) (PHB)[10] but not in poly(methyl methacrylate) (PMMA)[11] after aging below T_g. It has been suggested[8] that it may be related to volume relaxation, which has been shown to occur under similar conditions. This phenomenon is attributed to the progressive relaxation of the glass to the equilibrium liquid state. However, to our knowledge, a quantitative description of the relaxation phenomenon in PC has not been reported.

EXPERIMENTAL

PC with $M_w = 6.4 \times 10^4$ supplied by Aldrich (Milwaukee, WI, USA) was used in this study. The samples in the form of films were prepared by casting a PC solution (1% w/v) in dichloromethane onto a glass plate. The films were dried at 50°C under dynamic vacuum for 3 days and handled under watertight conditions. Thermal analysis was performed with a Perkin–Elmer differential scanning calorimeter, DSC-7. The calorimeter was calibrated using the fusion temperature of indium and zinc. These were taken as 156.6

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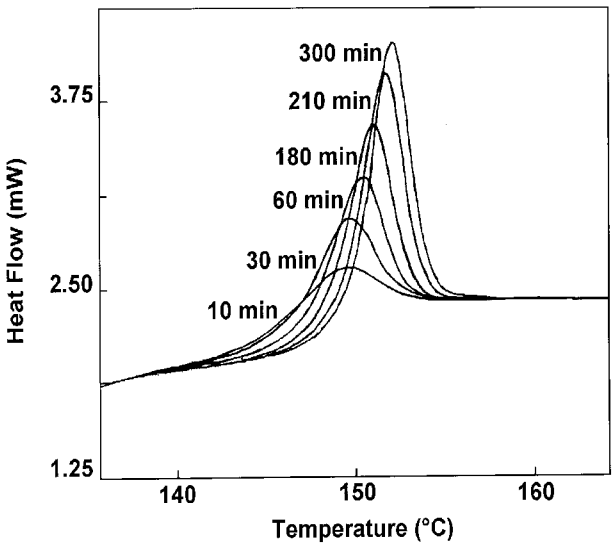

Figure 1 Representative thermograms of PC aged at 130°C for different periods of time (t) and later heated above T_g at a heating rate of 10°C/min.

and 419.5°C, respectively. The thermal response from the enthalpy of fusion of indium was taken to be 28.45 J/g. Samples of 10 mg, encased in aluminum pans, were used. All samples were heated previously in the DSC from 50 to 280°C at 10°C/min. Then they were cooled to the aging temperature (T_a) at a rate of 50°C/min. After a given aging time (t), the samples were heated again above the T_g at 10°C/min and the aging enthalpy $\Delta H_t(T_a)$ was recorded. The samples were aged at different temperatures, up to 30°C below T_g. The aging enthalpy $\Delta H_t(T_a)$ was measured from the difference between the integrated specific heat curves of the aged and unaged samples.

RESULTS AND DISCUSSION

As shown in Figure 1, the step change in the specific heat characteristic of the transition was accompanied by an aging endotherm which increased with aging time. It is noted that in all experiments, at a given temperature, both endothermic peaks and T_gs increased with aging time. The temperature shift observed was 2.5°C over the aging times studied. For a given T_a, it is observed that $\Delta H_t(T_a)$ increases with the t.

Following the approach proposed by Cowie and Ferguson,[12] the extent of relaxation $\phi_{Ta}(t)$ toward equilibrium at T_a is defined by

$$\phi_{T_a}(t) = 1 - \Delta H_t(T_a)/\Delta H_\infty(T_a) \quad (1)$$

where $\Delta H_\infty(T_a)$ is the value of $\Delta H_t(T_a)$ at $t = \infty$. This is when the glassy material reaches the equilibrium state at T_a.

Here

$$\phi_{T_a}(t) = \exp[-(t/\tau)^\beta] \quad (2)$$

is the Williams-Watts function[13] with τ an average relaxation time. The parameter β measures the breadth of the spectrum of these relaxation processes ($0 < \beta < 1$). The exact mathematical form of the function $\phi_{T_a}(t)$ is given in the reference.[13] From eqs. (1) and (2), one gets

$$-\mathrm{Ln}[1 - \Delta H_t(T_a)/\Delta H_\infty(T_a)] = At^\beta \quad (3)$$

where $A = (1/\tau)^\beta$. From the values of $\Delta H_t(T_a)$ obtained from the enthalpy curves, the parameters $\Delta H_\infty(T_a)$, β, and τ were determined. This was achieved by fixing $\Delta H_\infty(T_a)$, and through a power curve-fitting regression the values of τ and β and the corresponding correlation coefficient r were found. The value of $\Delta H_\infty(T_a)$ was then varied and the curve-fitting process was repeated. This gave another set of values of τ, β, and r. By this method the values of $\Delta H_\infty(T_a)$, τ, and β that gave the best coefficient r were taken from the regression.

For each aging temperature, the accepted values of $\Delta H_\infty(T_a)$, τ, and β were those that gave a correlation coefficient r higher than 0.99 (see Table I). As can be seen from Table I, the average calculated value of the parameter β is found to be 0.58 ± 0.06. A plot of equilibrium aging enthalpy $\Delta H_\infty(T_a)$ vs. aging temperature (T_a) is shown in Figure 2. The data points can be fitted by a straight line of the form

Table I Values of the Parameter $\Delta H_\infty(T_a)$, τ, β, and r Obtained for Different Aging Temperatures in Polycarbonate of Molecular Weight 64,000 g/mol

T_a (°C)	$\Delta H_\infty(T_a)$ (J/g)	τ (min)	β	r
120	5.33	2658	0.63	0.997
125	3.95	635	0.58	0.998
130	2.70	173	0.64	0.990
135	2.23	88	0.52	0.999

$$\Delta H_\infty(T_a) = -0.21T_a + 30.46 \quad (4)$$

From eq. (4), we get T_a = = (144.33 ± 2) °C when $\Delta H_\infty(T_a) = 0$, which occurs at the temperature T_g. Under this condition, the last equation can be rearranged as:

$$\Delta H_\infty(T_a) = 0.21(144.33 - T_a) \quad (5)$$

These results are consistent with the measured values of ΔC_p and T_g which are (0.21 ± 0.02) J/K · g and (146.0 ± 0.5)°C, respectively at a heating rate of 10°C/min. It can therefore be concluded that the relationship

$$\Delta H_\infty(T_a) = \Delta C_p(T_g - T_a) \quad (6)$$

proposed in reference[5] is valid for polycarbonate over the temperature range studied.

The logarithmic dependence of the relaxation time τ with T_a^{-1} is plotted in Figure 3. Linear behavior, as shown by the straight line, confirms that the relaxation process obeys the Arrhenius relation. From the slope, the activation energy is estimated to be 308 ± 50 kJ/mol. This is comparable to 260 ± 50 kJ/mol for poly(hydroxybutyrate), reported by Biddlestone et al.,[10] also obtained by DSC technique.

CONCLUSION

Polycarbonate shows annealing peaks on heating at different temperatures below T_g. It has been established that this behavior can be described by $\Delta H_\infty(T_a) = \Delta C_p(T_g - T_a)$. The relaxation process below T_g obeys Arrhenius law with an activation energy of 308 ± 50 kJ.mol^{-1}.

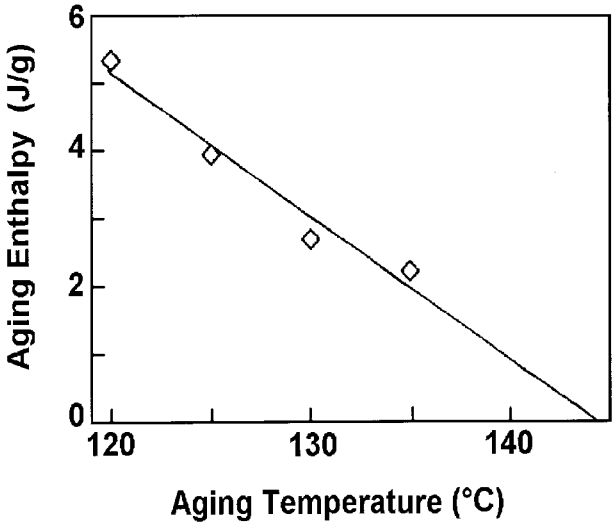

Figure 2 Equilibrium aging enthalpy $\Delta H_\infty(T_a)$ vs. aging temperature T_a.

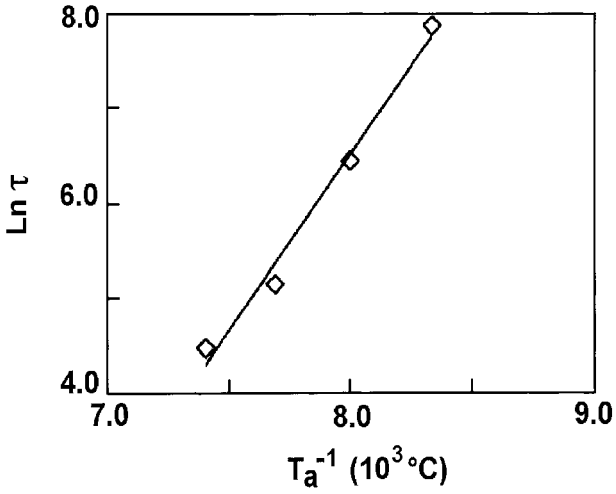

Figure 3 Arrhenius plot of ln τ against T_a^{-1}.

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