

Physical Aging of High-Performance Thermoplastics: Enthalpy Relaxation in PEK-C and PES-C

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SYNOPSIS

The developments of physical aging in phenolphthalein poly(aryl-ether-ketone) (PEK-C) and poly(aryl-ether-sulfone) (PES-C) with time at two aging temperatures up to 20 K below their respective glass transition temperatures ($T_g = 495$ and 520 K) have been studied using differential scanning calorimetry (DSC). Substantial relaxation within the aging course of several hours were observed by detecting T_g decreasing during physical aging process at the two aging temperatures. The relaxation processes of both polymers are extremely nonlinear and self-retarding. The time dependencies of their enthalpies during the initial stages of annealing were approximately modeled using the Narayanaswamy-Tool model. The structure relaxation parameters obtained from this fitting were used to predict the possibility of physical aging occurring at their respective using temperatures. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It has been known for many years that amorphous glassy polymers are not in the thermodynamic equilibrium state at temperatures below their glass transition temperatures (T_g).¹ A gradual approach to equilibrium can take place when the glassy polymers are stored or used at temperatures well below the glass transition. This process toward thermodynamic equilibrium is called structure relaxation or generally physical aging. This relaxation occurs more rapidly at temperatures close to T_g than at temperatures well below T_g . During this relaxation process, a large number of properties are affected, including but not restricted to density, enthalpy, entropy, creep compliance, modulus, dielectric permittivity, and electrical conductivity. Among these properties, enthalpy is a convenient property with which to monitor physical aging because of the availability of accurate and sensitive differential scanning calorimetry (DSC) instruments. Enthalpy lost during the aging process is recovered during reheating the aged sample to above T_g , and the en-

thalpy difference ΔH (enthalpy relaxation) between the original and the annealed (relaxed) glass is one of the simplest indication of the structure changes on annealing. But uncritical use of results from this type of apparatus can be very misleading. The true value can only be obtained by allowing for the decrease of T_g with annealing.²

At the present time we have investigated the effects of physical aging on the relaxation of enthalpies of two new high-performance thermoplastics phenolphthalein poly(aryl-ether-ketone) (PEK-C) and poly(aryl-ether-sulfone) (PES-C), which were developed in Changchun Institute of Applied Chemistry in China, by detecting the T_g variation during relaxation process. They are amorphous polymers with high T_g values ($T_g = 495$ and 520 K, respectively) and have been identified as excellent engineering thermoplastic matrix resins of high-performance composites since they were developed because of their high-temperature resistance, better solubility in certain solvents, and more economical in cost. Concerning the question of whether during the course of normal use physical aging will lead to sufficient changes in those properties to affect the desired behaviors of the glass polymers, in this study we focus on the objective to model the time and temperature dependencies of the observed kinetics

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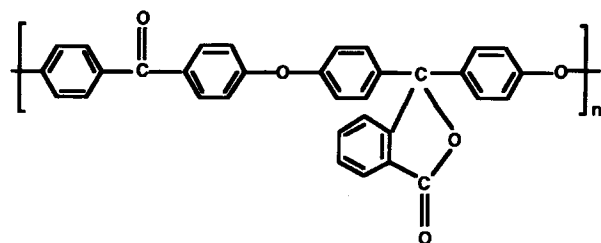
of the physical aging process and use the kinetic parameters so derived to predict the probable extent of physical aging after long periods under the normal use conditions. Because of the proximity in the chemical structure, the similar aging behavior between these two samples are expected. Future work to include physical aging in the blends based on their miscibility is in progress.

EXPERIMENTAL

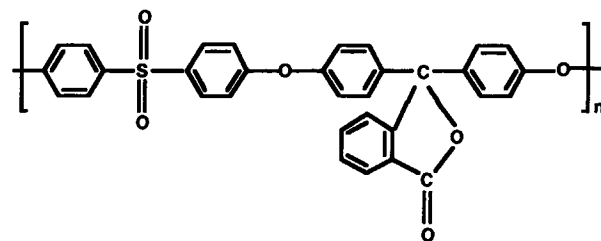
Materials

PEK-C and PES-C are commercially available in China. The reduced viscosities of the materials used in this study are 0.49 and 0.45 dL/g, respectively, in chloroform at 298 K and their chemical structures are as follows:

PEK-C



PES-C



Sample Preparation

Both materials in the form of powders were extruded and pelletized with a twin-screw extruder. Before extrusion the materials were dried in a vacuum oven at 393 K to erase any moisture and any solvent residuals. These pellets were dried again and molded into about 2 mm thick sheets with the hot press in our laboratory. The sheets were then cut into small disks with an official punch for enthalpy relaxation measurements and sealed in the standard aluminum crucibles.

Thermal Analysis

A Mettler differential scanning calorimetry, model DSC 30, was used to carry out the thermal analysis. The temperature scale and the energy output of the calorimeter were calibrated with melting of indium. This calibration was performed frequently. The heating rate of 10 K/min was applied in every case. After each measuring scan, the blank test which used two empty standard crucibles was followed using the same experimental conditions. From both of the above scans, the specific heat (C_p) as a function of temperature could be determined. The heating scans covered the temperature range of 373–593 K. But the specific heats were calculated only for the temperature interval of 433–573 K for both materials. All the aging processes were performed inside the calorimeter.

Isothermal Approach

The experimental procedures consisted of heating the samples of PEK-C and PES-C to 515 and 545 K, respectively (about 20 and 25 K above their respective T_g) and keeping at this temperature for 10 min to erase any prethermal historic effects. The samples were then quenched at 100 K/min with the liquid nitrogen equipment attached with DSC to the aging temperature T_a and annealed at this temperature for different aging times (t_a). After this time passed, the sample was quenched again at 100 K/min to 373 K and then was reheated at 10 K/min to 593 K. The heating scan performed with $t_a = 0$ (no aging took place) was regarded as the reference scan to calculate the T_{g0} for unaged sample.

RESULTS AND DISCUSSION

Glass Transition Temperature

The glass transition temperature of the material was determined in this work as the intercept of the liquid and glass segments of the enthalpy vs. temperature curves of the scans by transformation of DSC data as had been described many years before.²⁻⁴ It gives accurate values of T_g , and the obtained T_g in this way also coincides with the value of the fictive temperature (T_f) in the glass.⁵

Figure 1 shows schematically how the T_g 's are determined for both quenched (unaged) and well-annealed samples by measuring the change in enthalpy as they are reheated through the transition region.

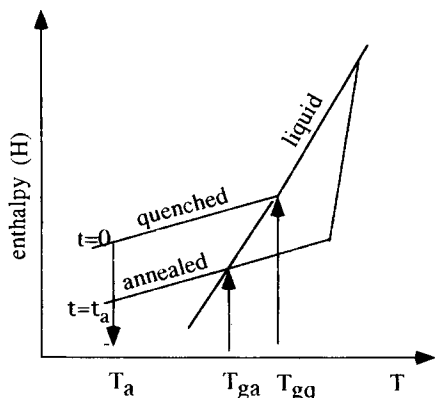


Figure 1 Schematic diagram of determining the glass transition temperatures (T_g) for both quenched and annealed samples.

Activation Energy for Structural Relaxation

In Figures 2 and 3 are shown the C_p (specific heat) traces for heating both samples at 10 K/min through the glass transition region immediately after rate cooling from the equilibrium above the glass transition at several different cooling rates (For the sake of clarity, only three are shown in both figures). Figure 4 shows the corresponding Arrhenius plots of cooling rate vs. glass transition temperature T_g for both materials. As explained before,⁵ from the slopes of these two straight lines in this plot we can calculate the average activation energy ΔH° for both samples which controls the structure relaxation very close to equilibrium in the glass transition region.

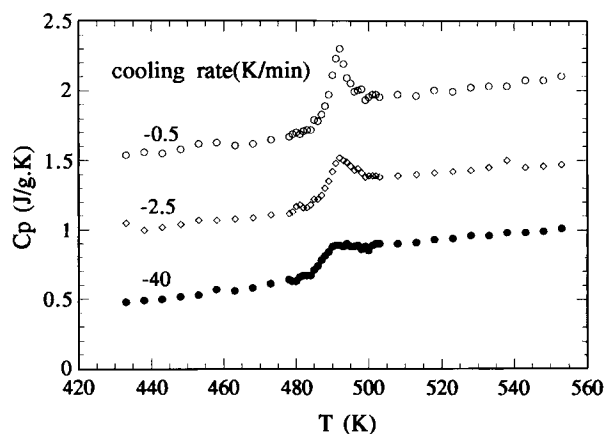


Figure 2 C_p variation of PEK-C with temperature measured at 10 K/min heating rate after cooled at different rates from equilibrium. (The curves of 2.5 and 40 K/min have been shifted downward 0.5 and 1.0 J/g K, respectively.)

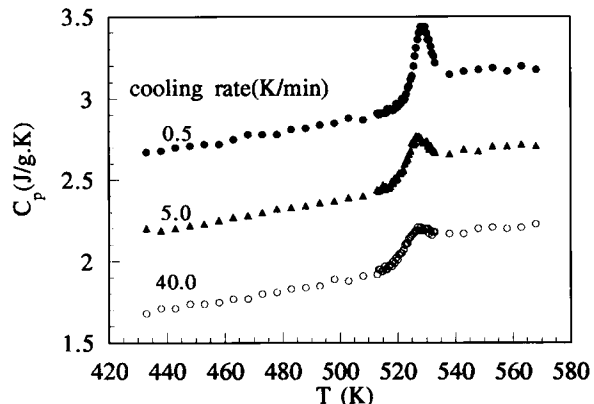


Figure 3 C_p variation of PES-C with temperature measured at 10 K/min heating rate after cooled at different rates from equilibrium. (The two top ones have been shifted upward 1.0 and 0.5 J/g K, respectively.)

$$d \ln|q|/d(1/T_g) = -\Delta H^\circ/R \quad (1)$$

where R is the ideal-gas constant. The value of ΔH° calculated according to Eq. (1) and Figure 4 are 1760 and 1012 kJ/mol for PEK-C and PES-C, which are comparable to those which have been observed elsewhere.⁶

Isothermal Aging

Figures 5 and 6 show the C_p variation measured after sub- T_g aging of PEK-C and PES-C at one of the two aging temperatures (For clarity only one temperature value is shown for each sample, i.e. $T_a = T_g - 10$ for PEK-C and $T_a = T_g - 20$ for PES-C) with the various aging times (t_a). They are typical DSC plots of polymeric materials which were initially cooled slowly through the glass transition region or

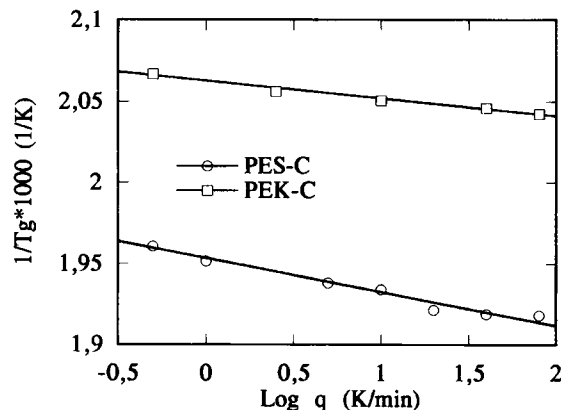


Figure 4 T_g variation with the cooling rate for PEK-C and PES-C.

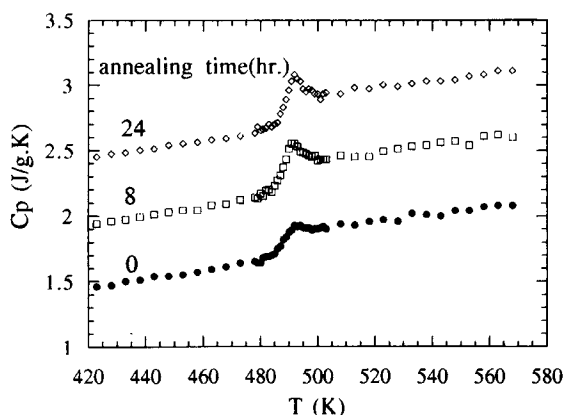


Figure 5 C_p variation with the temperature for PEK-C aged at 483 K ($T_g - 10$) for different times. (The two up ones have been shifted upward 1.0 and 0.5 J/g K, respectively.)

equilibrated above T_g and followed by a sub- T_g aging not far below T_g . With increasing aging time the maximum in the C_p curve increases in magnitude and shifts to a higher temperature. This is ascribed to the fact that the decrease in enthalpy during annealing is recovered during reheating to above the glass transition, and this recovery is usually manifested as a maximum in the heat capacity at temperatures ranging from well below to near the upper edge of the glass transition range.⁶⁻⁸

In Table I are listed the glass temperatures $T_g(t)$ of both samples calculated via the procedure provided by Richardson and Savill² from the enthalpy vs. temperature curves after annealing for various times at our two respective isothermal annealing temperatures. T_{g0} is that of the directly cooled sample from above T_g . It should correspond to the T_g of the sample at the beginning of the sub- T_g isothermal aging process.

In Figures 7 and 8 the $T_g(t)$ data of Table I are plotted vs. time at two aging temperatures. All these curves for PEK-C and PES-C are a dramatic illustration of the nonlinear (or self-retarding) character of the structure relaxation process, i.e., the strong dependence of the rate of physical aging on T_g . A marked drop in T_g takes place within several hours at these two aging temperatures for both samples. The very initial rate of aging is faster at the higher aging temperature (T_a) (T_g decreases more rapidly) in both cases. This is not surprising for physical aging is a denser packing process of molecular chains and a high T_a can accelerate it. But after a little longer time (about 48 h for both cases), the T_g values of the glass at lower T_a have nearly caught up with those of higher T_a which showed the strong depen-

dence of the aging rate on the distance from equilibrium, i.e., on the $T_g - T_a$. Beyond this time, very little further change occurs in T_g for both samples at the higher T_a . It is expected that after infinite time, these two glasses will reach equilibrium when the $T_g(t)$ gets to their respective T_a . It is suggested intuitively that the aging temperature can only affect the initial aging rate significantly. After a limited time (which varies with aging temperature), the relaxation process will get very slow until it reaches thermodynamic equilibrium, i.e., when $T_g \rightarrow T_a$.

Approximate Modeling of Physical Aging

Over the past 20 years or so, a number of phenomenological models have been developed and have been notably successful in describing many features observed experimentally in a wide variety of glasses.⁹⁻¹⁰ One of them,¹⁰ the Tool-Narayanawamy model, which was a recognition of the major contribution of these two workers, was employed in this work in approximate fashion to analyze the data of higher aging temperatures in Figures 7 and 8, respectively.

The structure of a glass with the glass transition temperature T_g is presumed to be describable in terms of a number n of order parameters, each of which can be associated a glass temperature T_{g_i} . The averaged, experimentally measured glass temperature is given by

$$T_g = \sum_{i=1}^n g_i / T_{g_i} \quad (2)$$

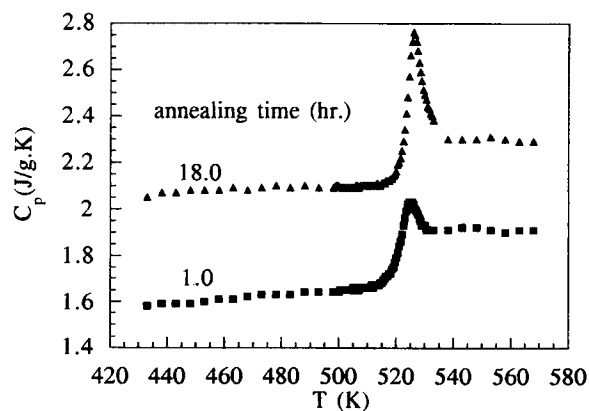


Figure 6 C_p variation with the temperature for PES-C aged at 498 K ($T_g - 20$) for different times. (For clarity only two were plotted and the up one has been shifted upward 0.5 J/g K.)

Table I Variation of Calculated T_g of Both Samples with the Aging Time at Two Different Aging Temperatures

Aging Time (h)	PEK-C		PES-C	
	T_g (K)		T_g (K)	
	$T_a = T_g - 10$	$T_a = T_g - 20$	$T_a = T_g - 10$	$T_a = T_g - 20$
0	494.39	494.39	519.92	519.92
0.5	492.8	—	—	—
1	491.81	492.97	516.95	518.70
2	490.5	491.34	514.57	516.45
4	489.05	490.06	513.75	514.75
6	—	—	—	513.04
8	488	488.88	—	—
15	—	—	511.93	—
18	—	—	—	511.03
24	486.88	487.28	510.03	—
48	486.2	486.28	509.04	509.45
64	—	—	—	508.86
96	—	—	508.58	507.55

where g_i is a weighting coefficient, it gives the fractional contribution of the i th order parameter to the average glass temperature. If starting at time 0, the glass is annealed isothermally at temperature T_a , the time dependence of T_g is given by

$$T_g(t) = T_a + \sum_{i=1}^n g_i [T_{g_i}(0) - T_a] \times \exp\left[-\int_0^t dt/\tau_i(t)\right] \quad (3)$$

where $T_{g_i}(0)$ is the initial value of T_{g_i} ; τ_i is the relaxation time governing the relaxation of the i th or-

der parameter. It depends both on temperature T (T_a in this study) and on structure [i.e., on $T_g(t)$] and can be calculated as follows:

$$\tau_i = A_i / \exp[x \Delta H^\circ / RT_a + (1 - x) \Delta H^\circ / RT_g(t)] \quad (4)$$

where ΔH° is an apparent activation energy and x ($0 \leq x \leq 1$) is a parameter defining the relative contribution of aging temperature and structure to the relaxation time τ_i ; R is the ideal-gas constant.

Here we regard the relaxation taking place within our experimental time range as only the initial stage of the total relaxation process, and after this time interval the relaxation process will get very slow. As

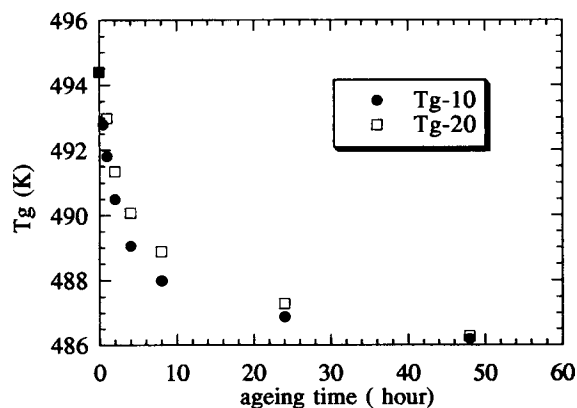


Figure 7 Variation of T_g with the aging time for PEK-C at two different aging temperatures.

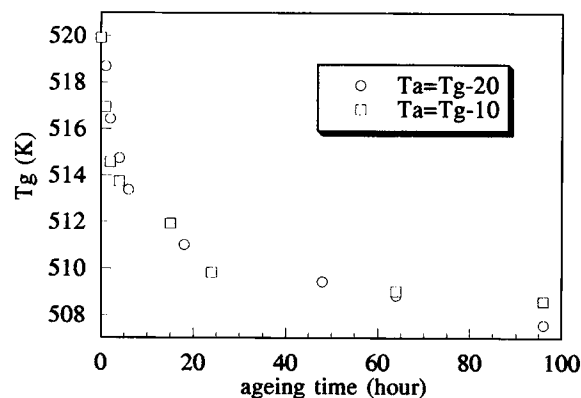


Figure 8 Variation of T_g with the aging time for PES-C at two different aging temperatures.

explicated in Ref. 10, we have made two approximations here: the first, we assume that during the initial stage (about 24 h for both materials at $T_a = T_g - 10$) only the first-order parameter (T_{g_1}) has changed and that the other order parameters (T_{g_2} , T_{g_3} , ..., T_{g_n}) have not departed from their initial values. So Eq. (3) becomes

$$T_g(t) = T_a + g_1(T_{g_1}(0) - T_a)\exp\left[-\int_0^t dt/\tau_1(t)\right] + \sum_{i=2}^n g_i[T_{g_i}(0) - T_a] \quad (5)$$

And second approximation, by considering the difference ($T_{g_0} - T_a$), is large compared to any likely differences between $T_{g_i}(0)$ values in Eq. (5), we can make a further assumption that $T_{g_i}(0) = T_{g_0}$ for all i . We note that all the g_i must sum to unity; then Eq. (5) can be written:

$$T_g(t) = (1 - g_1)T_{g_0} + g_1T_a + g_1(T_{g_0} - T_a)\exp\left[-\int_0^t dt/\tau_1(t)\right] \quad (6)$$

The aging data of table I and in Figures 7 and 8 at $T_a = T_g - 10$ for both samples have been fitted using Eqs. (4) and (6), and the obtained parameters are:

PEK-C:

$$g_1 = 0.72A_1 = 1.0 \times \exp(-434) \text{ h} \\ \Delta H = 1760 \text{ kJ/mol} \quad x = 0.467 \quad (7)$$

PES-C:

$$g_1 = 0.83A_1 = 5.6 \times \exp(-236) \text{ h} \\ \Delta H = 1012 \text{ kJ/mol} \quad x = 0.52 \quad (8)$$

The ΔH° values were calculated using Eq. (1) and the slopes of the two straight lines in Figure 4, while g_1 values were selected to correspond to the 72% relaxation observed in the initial stage at $T_a = T_g - 10$ annealing for PEK-C and 83% for PES-C. A_1 and x were chosen using an iterative computer program to minimize the standard deviation of the experimental $T_g(t)$ values from the calculated curve. The integral in Eq. (6) was evaluated numerically,

the time steps were obtained by dividing each experimental time interval into 10 equal intervals.

The solid curves in Figure 9 are those for both samples at $T_a = T_g - 10$ K calculated from Eqs. (4), (6), (7), and (8). It is obvious that the agreement between the experimental points and the fitting curve is good and the standard deviation of $T_g(t)$ from the best-fit curve are 2.16 and 1.79 K for both samples, i.e., within experimental errors.

Prediction of the Possibility of the Physical Aging Effects at Service Temperatures

Both materials will be used in high-temperature environments. So the enthalpy relaxation with the time will affect many properties of the materials. Here we use Eqs. (4), (6), (7), and (8) to predict the enthalpy relaxation (physical aging) effects on the variation of T_g 's of PEK-C and PES-C at fixed temperature, e.g., 423 and 443 K, respectively, which were manufactured at a cooling rate which will be met in real the manufacture process. The T_{g_0} values for the different cooling rates can be obtained using extrapolation of the solid lines in Figure 4. For the rapidly cooled sample, e.g., 10^6 K/min, which is of the order of cooling rate during fiber drawing process, and at 423 K of service temperatures for PEK-C, it will take more than 10^{10} h (about 10^6 years) when the physical aging occurs ($\Delta T_g = 1$ K). In the case of PES-C at 443 K, it needs about 10^5 h (11.4 years) for the T_g to decrease 1.0 K as regards its T_{g_0} . On the basis of current results, we can reasonably conclude that physical aging will not be a problem at these two temperatures for their applications during the designed lifetime. Of course, the change of T_g is not the only effect caused by enthalpy re-

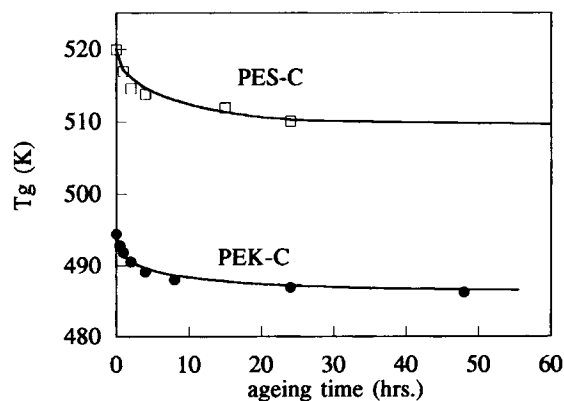


Figure 9 Comparison between model fitting curve and experimental points for PEK-C and PES-C, respectively, at the aging temperature of $T_g - 10$.

laxation. Some other property changes accompanying the enthalpy relaxation as mentioned in the introduction should also be taken into account during the course of normal use. It is also necessary to model the variation of the other properties during enthalpy relaxation. The correlation using the parameters obtained here with the variation of other properties, e.g., dimension stability, will be carried out in the future.

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