

Effect of Physical Aging on the Microstructure and Dynamic Mechanical Properties of Poly(ether sulfone) Copolymer

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ABSTRACT: Effects of physical aging on the submicroscopic structure and dynamic mechanical properties of amorphous poly(ether sulfone) copolymer film were studied by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and electron-microscopy measurements. Heat flow responses were measured after annealing the amorphous samples obtained, by quenching the melt into an ice-water bath close to but below the glass transition temperature. The extent of aging is related to the supercooling from the glass transition temperature and to the aging time. The activation energy of the aging process was estimated by the Williams–Watt expression (Williams and Watts, *Trans Faraday Soc* 1970, 66, 80). A systematic study of the influence of aging on the dynamic mechanical properties

of poly(ether sulfone) copolymer has also been made. During isothermal annealing, the increase of the temperature of $\tan \delta$ peak for the α and β' relaxation with aging time has been observed. The aging in the zone of the β peak has also been investigated and an interpretation of the results was proposed on the basis of foregone theories. The result of electron-microscopy investigation indicates that poly(ether sulfone) copolymer has formed a local order structure during the physical aging. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 530–534, 2006

Key words: poly(ether sulfone) copolymer; microstructure; dynamic mechanical properties

INTRODUCTION

It is well known that changes in structure and material properties occur in amorphous polymers upon annealing below and close to the glass transition temperature. This time-dependent behavior has been attributed to the nonequilibrium nature of the glassy state; it is often referred to as physical aging and is discussed in terms of the free volume concept¹ and cohesional entanglement (CE) theory.² Physical aging is important in a narrow temperature range. Characteristically, physical aging is accompanied by a reduction in free volume and a retardation of molecular motion. Thus, a change in creep characteristics, an increased yield stress, and embrittlement of the polymer on impact are often experienced.³ These features give rise to considerable interest in the physical aging phenomenon and the corresponding structural changes accompanying it. At present, a number of experiments using different probes, whose characteristics were shown to be sensitive to the glass transition or the free volume of polymers, were reported in the literature.^{4–6} Poly(aryl ether sulfone)s are high perfor-

mance engineering thermoplastics and have attracted much attention due to their excellent mechanical properties, solvent resistance, and high thermal stability.⁷ Different poly(aryl ether sulfone)s and its copolymers have been developed for some applications.^{8–11} Copolymers of poly(ether sulfone) (PES) and poly(ether ether sulfone) (PEES) units made either as blocks or as random materials showed some improved properties.¹² Previous work carried out on other polymers has shown that the microstructure may govern the mechanical behavior of polymers. For a better understanding of physical aging and mechanical properties of PES copolymer, the effect of physical aging on the microstructure and dynamic mechanical properties should be investigated in full detail. The molecular aggregation effect associated with the physical aging process would also be discussed.

EXPERIMENTAL

Sample preparation

Poly(ether sulfone) (PES) copolymer was synthesized by one step reaction method, using 4,4'-dichlorodiphenyl sulfone (DCDPS), 4,4'-dihydroxydiphenyl sulfone (DHDPS), and hydroquinone (HQ) in sulfolane medium at 30% solid content under a nitrogen atmo-

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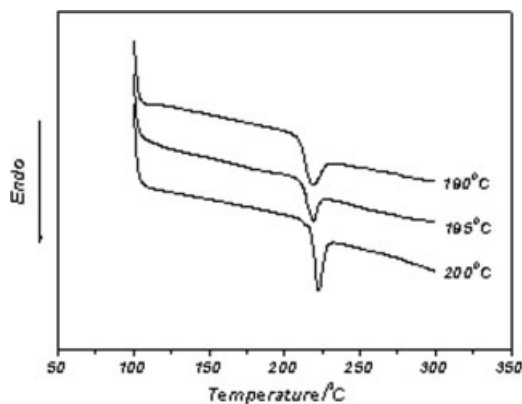


Figure 1 DSC curves of PES copolymer samples subjected to physical aging at different temperatures.

sphere. Detailed procedures of the synthesis routes have been described previously.¹³ PES copolymer with the HQ to DHDPS molar ratio (50/50) was selected for this study. The inherent viscosity of PES copolymer is 0.39 dL/g, when measured in dimethylformamide (DMF) at $(25.0 \pm 0.1)^\circ\text{C}$ using an Ubbelohde viscometer. The glass transition temperature measured by a Mettler Toledo DSC 821e was 215°C . Copolymer powder was pressed at 280°C under a pressure of 10 MPa for 2 min, followed by quenching in an ice-water bath to 1-mm thick amorphous sheets.

DSC and ADSC measurements

Mettler DSC 821e was used to measure the heat flow as a function of temperature. The calorimeter was previously calibrated with indium standards at a heating rate of $20^\circ\text{C}/\text{min}$. Only a brief review of the ADSC technique is given here. The temperature program consists of the conventional linear temperature rise with time ramp, which in the case of ADSC is modulated by a small sinusoidal perturbation. The modulated heat flow signal is averaged to obtain the total

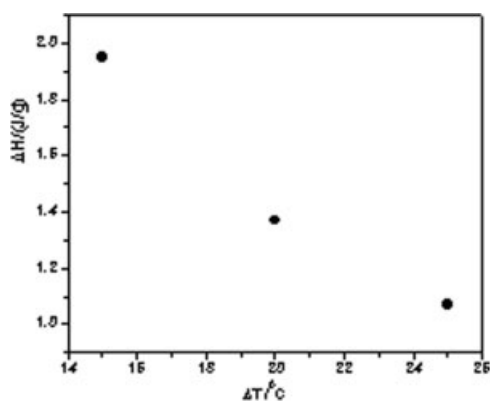


Figure 2 Dependence of the relaxation enthalpy of PES copolymer on the supercooling to T_g .

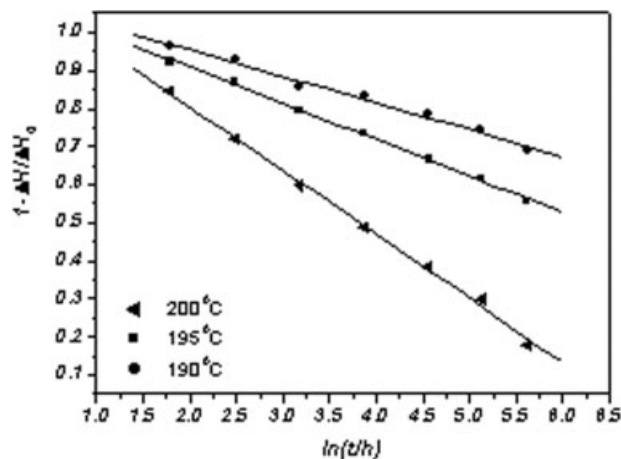


Figure 3 Semilogarithmic plot of the unaged extent with time, which shows the kinetic parameters of physical aging.

heat flow signal, which is equivalent to a normal DSC experiment. The amplitude of the cyclic response is measured by a Fourier transform technique and from this, a value for the heat capacity, called the cyclic heat capacity, is obtained. By multiplying this, the reversing signal is obtained. By subtracting this reversing signal from the total heat flow, the nonreversing signal is calculated. ADSC measurements were made at a heating rate of $2^\circ\text{C}/\text{min}$. An oscillation amplitude of 2°C and an oscillation period of 60 s were used throughout this investigation. The relaxation enthalpy was calculated using the nonreversing heat flow signal. PES copolymer samples were aged at 190, 195, and 200°C , and the aging time is assigned from 6 to 276 h.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out in the tension mode, using a viscoelastic analyzer (TA model Q800). Isochronal scans at 1 Hz were recorded

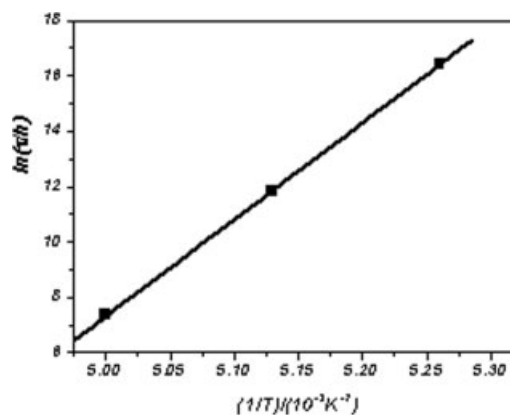


Figure 4 Plot of the $\ln \tau$ versus $(1/T)$, which gives the relaxation activation energy.

TABLE I
Physical Aging Parameters of PES Copolymer Sample

Supercooling ΔT (°C)	Relaxation time $\ln \tau$ (h)	Activation energy E_a (kJ/mol)
15	7.35	290.7
20	11.81	
25	16.4	

over a temperature range of -130 – 250°C at a scanning rate of $3^\circ\text{C}/\text{min}$.

Transmission electron microscopy

The transmission electron microscopy (TEM) instrument used was Hitachi model H-8100 (Hitachi). The acceleration voltage was 200 kV. The samples for transmission electron microscopic investigations were obtained via solvent casting from 5 wt % dichloromethane solutions at 25°C . Thus obtained bulk specimens were ultramicrotomed at -100°C , with a diamond knife, to sections of about 50-nm thickness, using Reichert-Nissei Ultracut-S Ultramicrotome.

RESULTS AND DISCUSSION

Physical aging of poly(ether sulfone) copolymer

The glass transition of the copolymer sample held at various temperatures close to but below the transition temperature was characterized by a marked endothermic peak as observed from the DSC trace on heating through the glass transition. The thermograms of the sample subjected to aging time 48 h from 190 to 200°C are shown in Figure 1. The relaxation enthalpy of the aged samples is strongly dependent upon the aging temperature (T_a) and time. As shown in Figure 2, the relaxation enthalpy of the copolymer sample decreases with the supercooling to T_g . This agrees with the segmental motion of the macromolecules, because the segmental motion rate of macromolecules is quick-

ened with the increase of aging temperature at the same aging time. The extent of the endothermic process increases logarithmically with time. The excess enthalpy developed at time t , ΔH_t , was obtained from the nonreversing heat flow signal. The maximum enthalpy change,^{14,15} ΔH_{max} , is

$$\Delta H_{\text{max}} = \Delta C_p(T_g - T_a) = \Delta C_p \Delta T \quad (1)$$

corresponding to equilibrium having been achieved at T_a , the aging temperature. The maximum difference in specific heat between the glass and the liquid, ΔC_p was $0.305 \text{ J g}^{-1} \text{ K}^{-1}$ for the unaged PES copolymer sample. The extent of physical aging at time t , $\Delta H_t/(\Delta C_p \times \Delta T)$, and the extent of the unaged portion, $[1 - \Delta H_t/(\Delta C_p \times \Delta T)]$, decrease logarithmically with time at each aging temperature. Figure 3 represents the semilogarithmic plot of the unaged extent and time. A good linearity relation between the unaged extent and the semilogarithmic of aging time was observed. These were used to define a relaxation time, τ ¹⁶:

$$[1 - \Delta H_t/(\Delta C_p \Delta T)] = A \ln(3t/2\tau) \quad (2)$$

Thus, the relaxation time at different temperatures during the aging process is obtained from the slope and the intercept of the plot of $[1 - \Delta H_t/(\Delta C_p \times \Delta T)]$ versus $\ln t$. The relaxation time during the aging process was observed to increase with the increase in supercooling. An Arrhenius form may be used to describe the relationship between the observed relaxation time, τ , and the activation energy of aging (E_a) over the limited temperature range of the measurements. A plot of $\ln \tau$ versus $1/T$ is shown in Figure 4, and the corresponding activation energy (E_a) is 290.7 kJ/mol. The physical aging parameters of PES copolymer are shown in Table I. To eliminate the probable and instrumental error, we repeated the physical aging experiments three times having a reproducibility higher than 90%.

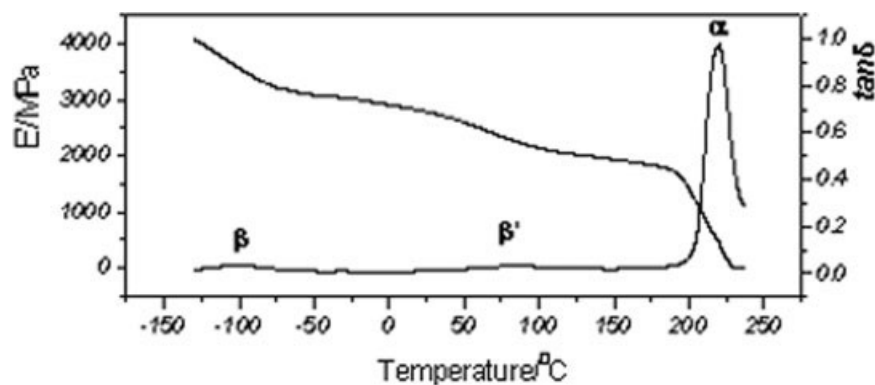


Figure 5 Typical dynamic mechanical behavior of the unaged PES copolymer sample.

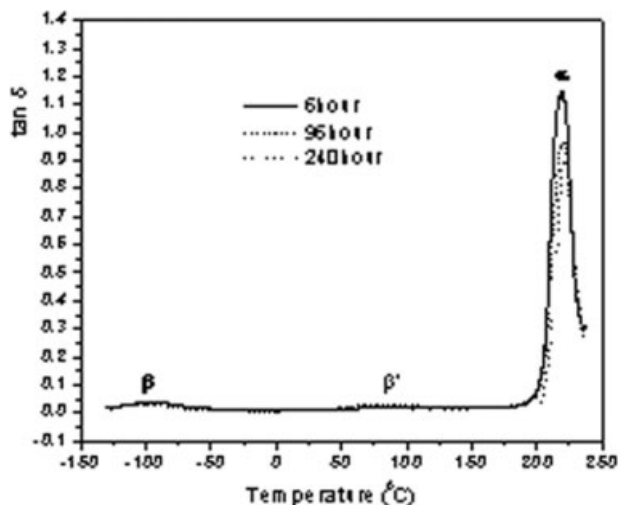


Figure 6 $\tan \delta$ -temperature curves of PES copolymers with different aging time.

Glass and subglass relaxations of poly(ether sulfone) copolymer

A typical dynamic mechanical spectrum of PES copolymer with temperature is shown in Figure 5. Three distinct loss maxima are observed and named as β , β' and α relaxation peaks from low to high temperature. The wide β relaxation peak is observed at about -100°C , and the α relaxation peak is found at 220°C . In addition to the β relaxation peak and the α relaxation peak, another relaxation peak in the range from 40 to 100°C , named as β' relaxation peak, is observed in the dynamic mechanical spectroscopies for the unaged specimens. According to previous reports,¹⁷ the low temperature mechanical relaxation in semirigid chain polymers is attributed to a local motion of phenylene units in the main chain. The very sharp loss

peak observed at 220°C is attributed to the molecular motion reflecting the transition from glassy to rubbery state. The β' relaxation is sometimes described and is attributed to the presence of higher disorder sites within the glassy polymer. The dependence of $\tan \delta$ for the specimens aged at 200°C for different time is shown in Figures 6 and 7. Comparing the figures with Figure 5, it is seen that the profiles of β and β' relaxation peak are slightly changed upon aging. Similar phenomena have been reported for poly(ether ether ketone) (PEEK).¹⁷ The location of $\tan \delta$ peak for the β' relaxation is changed largely by aging. But, the location of the β process is surprisingly less affected. Accordingly, the local motion of phenylene units in the main chains is not affected largely by physical aging. The glass transition temperature of copolymer (α relaxation) increases by physical aging. The temperature of $\tan \delta$ peak for the β' relaxation is also increased by physical aging. This is similar in appearance to the "structural relaxation" process that has been observed in rigid chain polymers.^{18,19} The mechanical loss in the β' relaxation region of these samples may be considered because of rearrangement of the main chain toward more rigid chain packing in amorphous region from a loose packing introduced by rapid quenching.

Morphology of molecular aggregation

Further, electron spectroscopy was applied to the heat treated PES copolymer thin section to investigate the effect of physical aging in the morphology of molecular aggregation. Figure 8 shows the results. Figures 8(a) and 8(b) are the perspective and diffraction micrographs, respectively. Figure 8(A) shows the micrograph of the untreated PES copolymer. The micrograph of the untreated PES copolymer reveals the

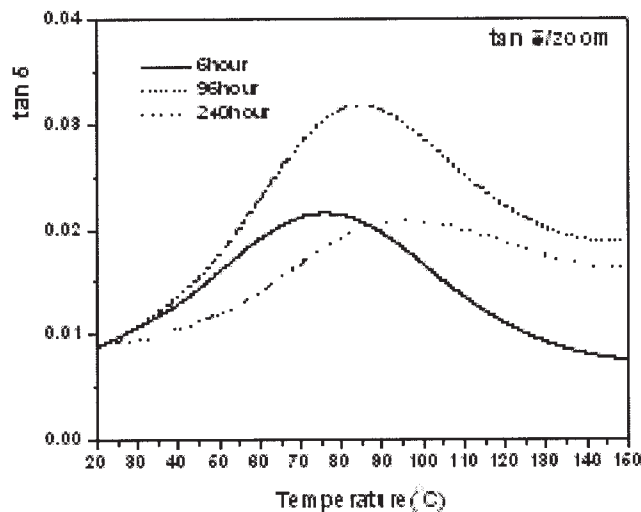
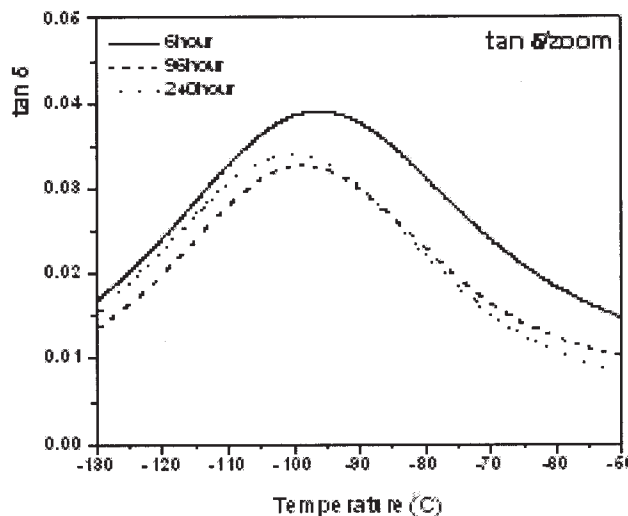


Figure 7

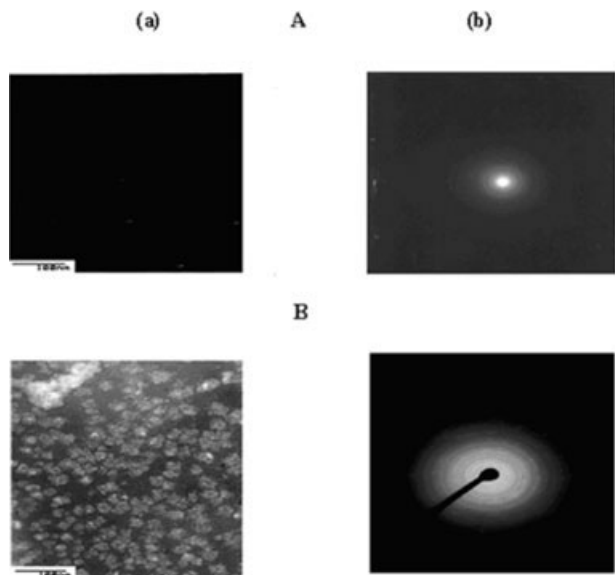


Figure 8 Diffraction pattern of the heat-treated PES Copolymer. A: untreated; B: heat treated at 200°C for 96 h; (a) perspective pattern; (b) diffraction pattern.

diffraction pattern which corresponds to an amorphous random structure of general amorphous polymers. Figure 8(B) shows the micrograph of the heat treated PES copolymer at 200°C for 96 h. The perspective pattern of the heat treated copolymer shows many bright clusters of about 20 nm compared with that of untreated copolymer sample. We think that some local order structures are formed after heat treating. Accordingly, the diffraction pattern of the heat treated copolymer has clear and stable diffraction ring. This suggests that the heat treated PES copolymer at 200°C for 96 h has a molecular aggregation and forms a short range order phase. However, the structure of the PES copolymer sample is "amorphous" both before and after annealing, when judged by the DSC and X-ray diffraction pattern. It has been suggested²⁰ that short-range reordering or "crystallization" might take place on annealing, which would not give rise to sharp Bragg reflections if the ordered regions remained very small. The short range order in "amorphous" materials can be characterized precisely by means of radial

distribution function (RDF) methods.²¹ The RDF experiment of heat treated PES copolymer will be reported in future.

CONCLUSION

Amorphous PES copolymer ages in an analogous fashion to other polymers observed previously and is associated with the kinetic nature of glass transition process. The extent of aging is related to the supercooling from the glass transition and the change in heat capacity between the glass and the liquid at the transition temperature, and the activation energy of the ageing process was evaluated.

The result of DMA showed that the glass and sub-glass relaxations of PES copolymer were affected by physical aging. Accordingly, the morphology of the heat treated copolymer was changed into a local order phase.

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