

Thermostimulated Current Characterization of Poly(ethersulfone)

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ABSTRACT: Two thermal analysis techniques, differential scanning calorimetry (DSC) and thermostimulated currents, are used to characterize two Poly(ethersulfones) (PESs) obtained with the same process by two different manufacturers. The glass transition temperature observed by DSC is the same for both PESs and equal to 235°C. When PES samples are heated above the glass transition temperature (250–260°C), one initially white and opaque PES (B) looks transparent while the other one (A) stays in the initial stage. The PES B is visibly degraded upon increasing at a lower temperature than PES A. Below the glass transition temperature, two complex relaxation modes α and β situated at +170–175 and –120°C, respectively, are observed. The analysis of the fine structure shows that they are constituted of elementary processes characterized by relaxation times following compensation laws. For PES A at high temperatures the cooperative movements are precursors of the glass transition. For PES B a double compensation phenomena reveals the biphasic character of the vitreous phase. The comparison between the two PESs reveals different microstructures that could be due to different processing conditions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 320–325, 2000

Key words: thermally stimulated currents; polyethersulfone; glass transition; dielectric relaxation; compensation law

INTRODUCTION

Aeronautic advanced composite materials are by now well-known substitutes for conventional structural materials such as steel and aluminum. Their characteristics generally include directional stiffness and strength, light weight, and corrosion resistance, and have provided designers with significant performance advantages.¹

The most employed materials to reach this aim are carbon fibers and epoxy resins. The matrix includes thermoplastic materials such as Poly-

(ethersulfone) (PES) to confer better impact strength.

The subject of this study is to determine whether two PESs synthesized with the same method but in different places (transfer of license) are equivalent. To achieve this purpose two thermal analysis methods are used: differential scanning calorimetry (DSC) to define the transitions and thermostimulated currents (TSC) for the dynamic analysis of the chain structure.

EXPERIMENTAL

Materials

Two PESs with hydroxy ending groups^{2,3} were synthesized with the same process under license

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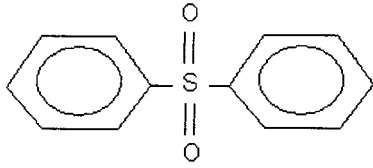


Figure 1 The chemical structure of PES.

but in different manufacturing plants. We designate the two PESs as A and B in this article.

Figure 1 presents the chemical structure of PES. They issued from the synthesis as a powder, compacted to form pellets of 1-cm diameter.

Methods

DSC

DSC measures the thermal flux emitted or absorbed during transitions. The thermograms were recorded on a DSC7 from Perkin Elmer. The temperature was varied from room temperature to 300°C at a scanning rate of 20°C/min. The glass transition temperature (T_g) was determined at the midpoint of the step in heat capacity.

TSCs

The sample was inserted between two capacitor plates and polarized for 2 min under a 250 kV/m voltage at a temperature of 180°C. Then it was quenched to -160°C to freeze the dipolar entities oriented by the static electric field. The sample was then short circuited. A linear heating of 7°C/min relaxed the oriented dipolar entities, which released the depolarization current that was measured by an electrometer.⁴ The thermograms were recorded through a TSC-RMA spectrometer.

Generally, in polymeric materials the TSC spectra are complex. For resolving such complex TSC spectra into elementary spectra, the procedure of fractional polarization was used.

In this case the sample was polarized at the polarization temperature (T_p) for 2 min under 250 kV/m. Then the sample was quenched down to the depolarization temperature (T_d) = $T_p - 5^\circ\text{C}$ to freeze the fractional polarization corresponding to relaxation time τ such that $\tau(T_p) < \tau < \tau(T_d)$. The depolarization current recorded during a usual TSC cycle gives an “elementary” spectra that can be analyzed in the hypothesis of a single relaxation time τ . Then T_p is shifted by steps of 5° in order to sweep the whole temperature range.

The temperature dependence of the different relaxation times is correctly described by the following Arrhenius equation:

$$\tau = \tau_0 \exp \frac{\Delta H}{kT} \quad (1)$$

where τ_0 is the preexponential factor, ΔH is the activation enthalpy, and k is the Boltzmann constant with⁵

$$\tau_0 \approx \left(\frac{h}{kT} \right) \exp \left(- \frac{\Delta S}{k} \right) \quad (2)$$

where h is Planck’s constant and ΔS is the activation entropy.

RESULTS

Transition Spectra

PES A and B have the same glass transition temperature (235°C) as shown in Figures 2 and 3, respectively, so we can conclude that the macroscopic thermal properties are analogous.

Complex Relaxation Spectra

For each PES two spectra are reported in Figures 4 and 5 to show the reproducibility of such complex spectra. Each spectrum exhibits two relaxation modes labeled β and α in the order of increasing temperatures:

1. at low temperature the β mode is situated at around -120°C as shown in Figure 4 and
2. at high temperature the α mode is observed at around $+170^\circ\text{C}$ for PES B and $+175^\circ\text{C}$ for PES A as shown in Figure 5.

In order to determine the origin of those modes, the elementary TSC spectra were recorded.

Fine Structure of Relaxation Spectra

Fractional polarizations allowed us to resolve the complex spectra into its elementary components.⁶ Figures 6 and 7 show as example of the elementary spectra isolated in PES A at low and high temperatures, respectively. Figure 8 gives as example of the Arrhenius diagram corresponding to the high temperature relaxation mode of PES A.

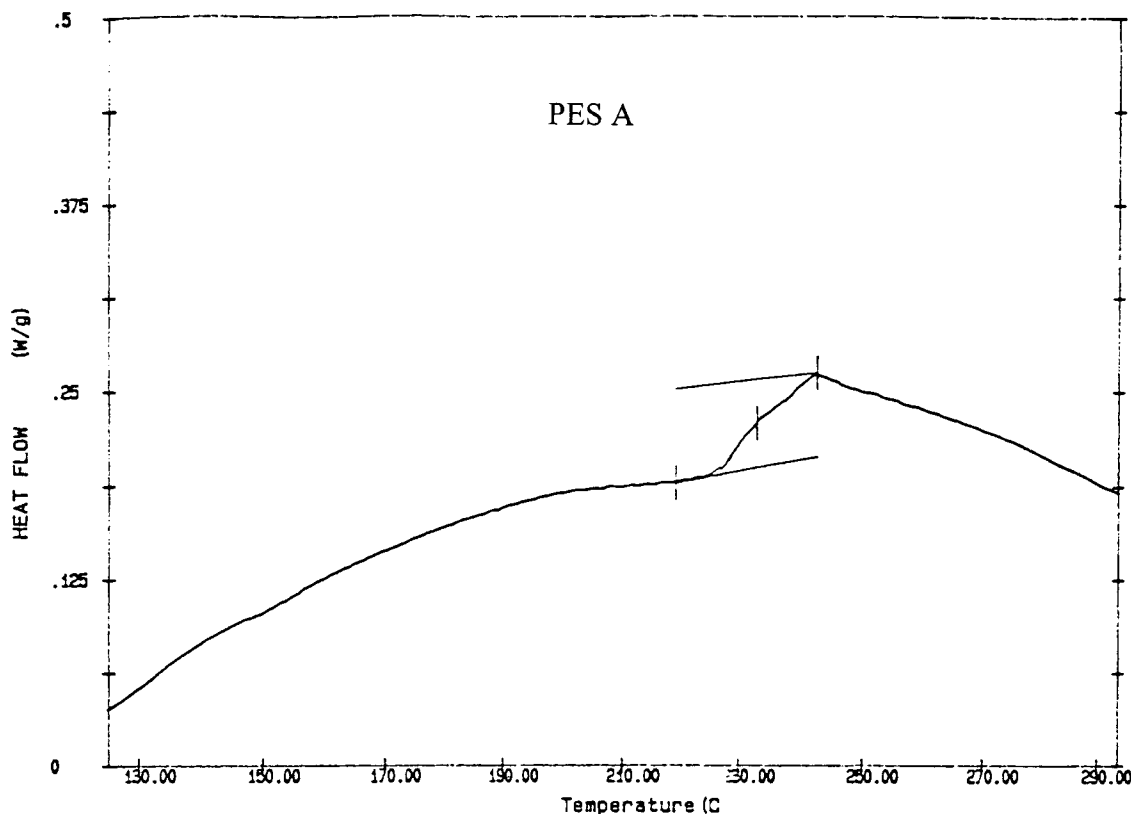


Figure 2 The DSC spectra of PES A.

The extrapolations of the variations of $\log \tau$ versus T^{-1} converge in one point (τ_c , T_c) designated as the compensation point⁷; at the compensation temperature $T_c = 270^\circ\text{C}$ all the relaxation times constituting this α mode are equivalent to the compensation time $\tau_c = 0.1$ s.

PES B has different behavior: for the elementary peaks isolated in the temperature range of $95\text{--}115^\circ\text{C}$ a "low temperature" compensation law was obeyed with $T_{cl} = 160^\circ\text{C}$ and $\tau_{cl} = 0.5$ s. For the elementary peaks isolated in the temperature range of $150\text{--}170^\circ\text{C}$ a "high temperature" compensation law was followed with $T_{ch} = 175^\circ\text{C}$ and $\tau_{ch} = 30$ s.

DISCUSSION AND CONCLUSION

We analyzed two PES samples giving different macroscopic observations. After heating at $20\text{--}30^\circ$ above the glass transition temperature, PES A stays opaque while PES B becomes transparent. DSC did not show any differences between

both samples characterized by the same glass transition temperature (230°C). TSC showed the existence of two types of molecular mobility: one in the glassy state and another around the glass transition temperature.

Molecular Mobility in Glassy State

At low temperature (-120°C) a complex β mode was observed in both PESs with the same characteristics. The analysis of its fine structure showed that it was constituted of elementary processes characterized by Arrhenian relaxation times. The preexponential factors remained of the order of magnitude of 10^{-13} s. According to eq. (2), because $(h/kT) \approx 10^{-13}$ s also, this means that $\Delta S \approx 0$. Moreover, activation enthalpies were of the order of magnitude of 0.5 eV. Both values indicated that this low temperature relaxation mode was due to localized molecular movements in the glassy state. The absence of notable differences in both PESs was explained by the lack of

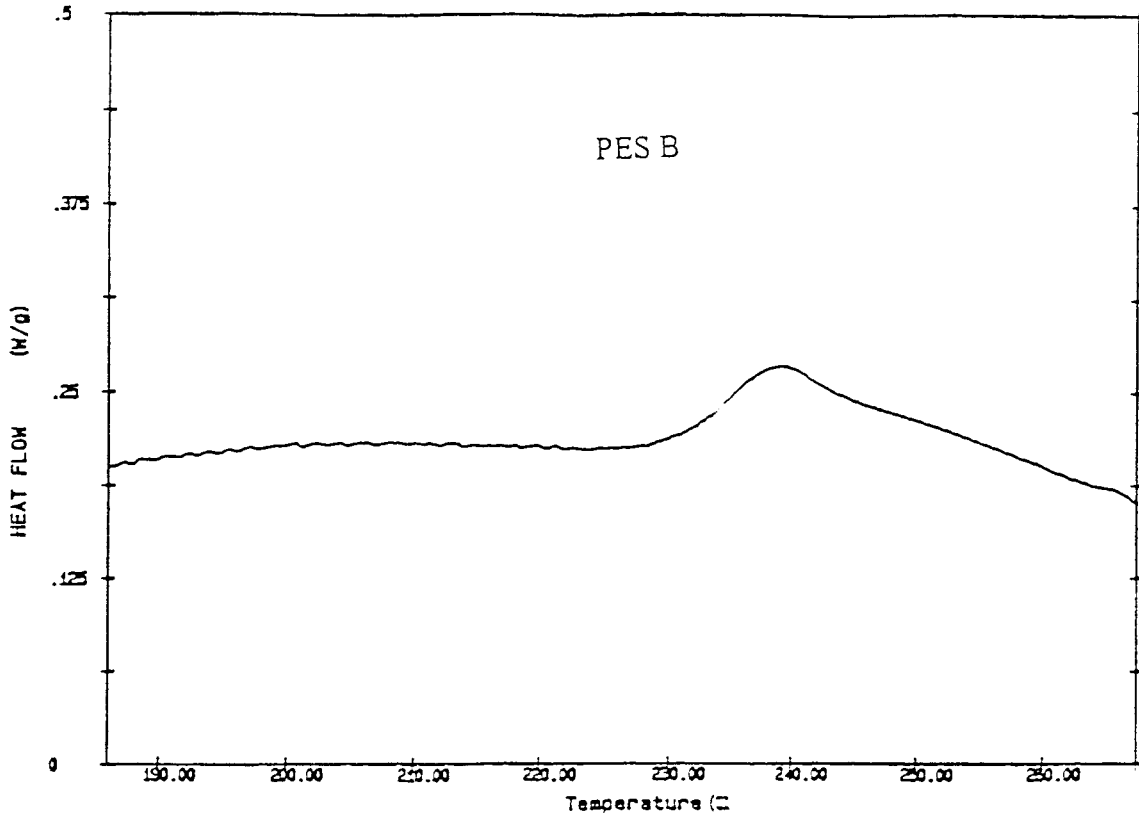


Figure 3 The DSC spectra of PES B.

influence of processing conditions at this local scale (<1 nm).

Molecular Mobility around Glass Transition Temperature

A high temperature relaxation mode, which was observed at around 170°C , was recorded in both

PESs. Its magnitude was 100 times higher than the one of the β relaxation mode. In addition to differences in magnitude, it was difficult to appreciate differences in the shape of the peaks of both PESs. The differences appeared in the analysis of the fine structure.

For PES A the Arrhenius diagram corresponding to the elementary processes isolated below the

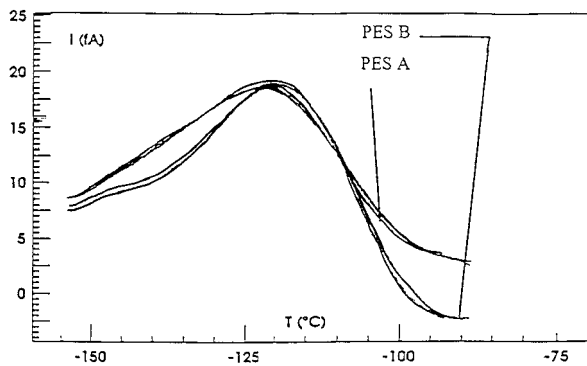


Figure 4 A comparison of low temperature TSC modes of PES.

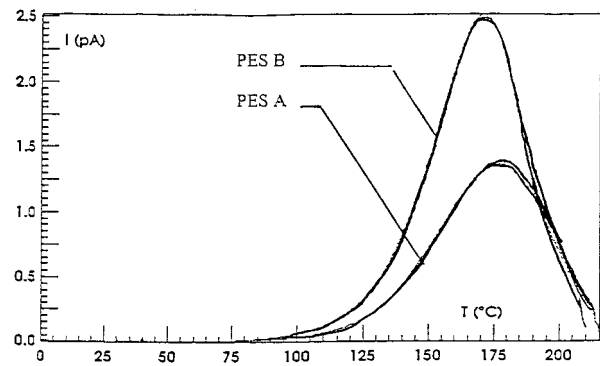


Figure 5 A comparison of high temperature TSC modes of PES.

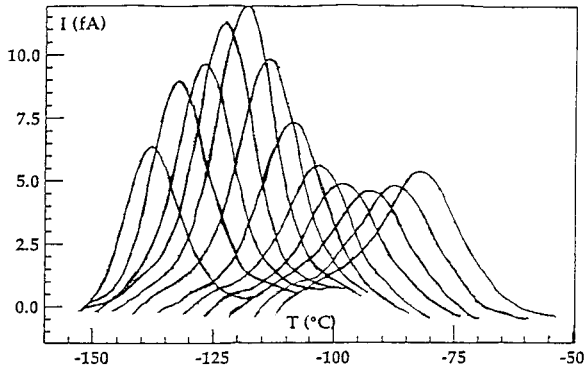


Figure 6 The low temperature elementary TSC spectra of PES A.

glass transition were characterized by relaxation times following a single compensation law as shown on Figure 8. Another representation of this behavior is given in Figure 9 where $\log \tau_0$ is plotted as a function of the activation enthalpy. The numbers indicate the polarization temperature (1 is for $T_p = 80^\circ\text{C}$). The single compensation law of PES A is reflected by the single compensation line while for PES B the two compensation lines reveal the existence of two compensation processes.

It is important to note that the compensation temperatures remained of the order of magnitude of T_g : they ranged between $T_g + 40^\circ$ for PES A and $T_g - 80^\circ$ for PES B. On the other hand the compensation times varied from 0.1 to 30 s. Those values confirm that the corresponding molecular mobility was associated with the glass transition.⁸

The compensation phenomena observed at a higher temperature in PES B implies a larger group of processes with activation parameters

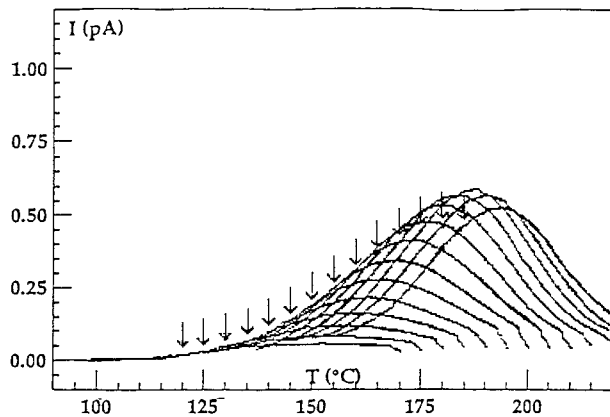


Figure 7 The high temperature elementary TSC spectra of PES A.

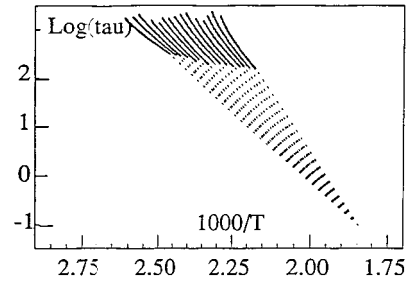


Figure 8 An Arrhenius diagram of the relaxation times of the high temperature TSC mode of PES A.

analogous to the ones of PES A. Those phenomena are attributed to the major relaxation mode associated with T_g . Note also that both submodes have analogous compensation times and thus activation entropies. Contrarily, the lower temperature submode of PES B has lower values of τ_0 and so higher values of ΔS . So the corresponding molecular mobility is located in more disordered domains.

The observation of such phase segregation between two amorphous phases might be assigned

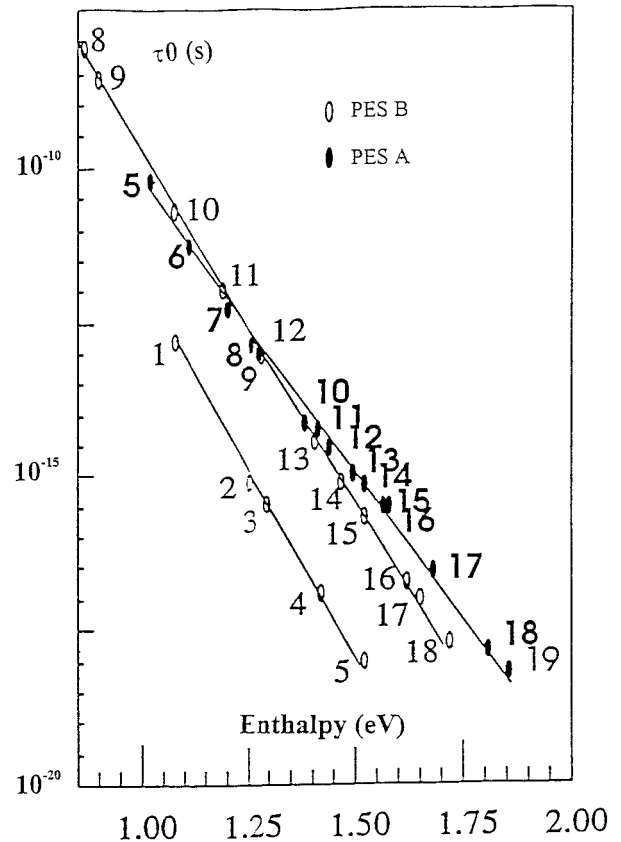


Figure 9 A comparison of compensation diagrams of PES A and B.

to different thermodynamic histories during processing. Indeed, during vitrification the temperature variation when crossing the glass transition was mainly responsible for the microstructure: quenching favors phase segregation while slow temperature variation gives a more homogeneous microstructure.

Structural differences are more important in polymers with flexible chains like PES.

Because we are dealing with differences between amorphous phases, to our knowledge there are no other techniques allowing the discrimination of such microstructures.

The molecular origin of the compensation law can be discussed with the model proposed by Hoffman et al.⁹ for paraffin. The value of the activation parameters reflects the size of the mobile sequences. Going from low to high temperatures, the elementary processes involve longer sequences. In fact, the compensation law reflects the cooperativity of the mode associated with the T_g .

Let us compare the highest values of the activation enthalpy of PES (1.5 eV) with the one of another thermostable polymer like Poly(etheretherketone)⁹ (5 eV); the lower value recorded for PES reflects its well-known high chain flexibility.

This peculiarity that allows us to use PES as plasticizer of polyepoxy is also involved in struc-

tural considerations. Indeed, we found two compensation laws in PES B that indicate the existence of a biphasic amorphous structure: less cohesive domains where a precursor relaxation submode is observed and the more cohesive amorphous phase where the major relaxation submode associated with the glass transition takes place.

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