Dielectric Spectroscopy of Polystyrene/Poly(ethylene oxide) Composites

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ABSTRACT: Dielectric spectra of composites of poly(ethylene oxide), PEO, in polystyrene, PS, have been obtained, as a function of frequency and temperature. The dispersion of a high-dielectric constant, low-glass transition temperature, semicrystalline polymer (PEO) in an amorphous, lower dielectric constant, high-T_g continuum (PS) has enabled the dielectric observation of four molecular relaxation processes in PEO. They are the α relaxation associated with the crystalline melt of PEO; two WLF type relaxations, β and β', which we speculate to be respectively associated with the onset of segmental motion and free-volume expansion of unrestricted amorphous PEO chains and with amorphous PEO chain segments tethered in crystallites; and a sub-T_g, γ relaxation associated with localized motions in the crystalline chain segments. The relaxations associated with the α and β' processes have not been previously observed dielectrically. In pure, neat PEO, the α and β' relaxations are obscured by dc losses. The dispersion of PEO as micron-sized and submicron phases in PS enables its full relaxation spectrum to be observed.

Introduction

In the course of efforts to elucidate aspects of morphology and phase distribution in composites of poly(ethylene oxide), PEO, in polystyrene, PS, dielectric spectra have been obtained, as a function of frequency and temperature. The dispersion of a high-dielectric constant, low-glass transition temperature, semicrystalline polymer (PEO) in an amorphous, lower dielectric constant, high-T_g continuum (PS) has revealed a multiplicity of relaxations in PEO which have not been previously seen dielectrically. Dispersion as micron-sized and submicron phases in PS does not, however, fundamentally alter the molecular relaxation characteristics of PEO.

Experimental Section

Materials. The polystyrene employed as the matrix in all composites was a polystyrene standard (Lot No. 61126) obtained from Pressure Chemical (Pittsburgh, PA). The manufacturer reports its number-average molecular weight to be 105 000 Da and its polydispersity to be 1.04. Poly(ethylene oxide) homopolymer employed in this study and referred to herein as PEO, without specification of molecular weight, was poly(ethylene glycol), molecular weight = 3400 Da, from Aldrich Chemical Co.

Sample Preparation. Composite films, of about 50 μm in thickness and comprised of 5% by weight of PEO in PS, were puddle cast onto glass substrates from cyclohexanone. The concentrations of the solutions were about 12% solids by weight. The glass substrates were warmed to 65 °C on an aluminum block during film formation to prevent crystallization of PEO prior to solidification of the PS matrix. Dried films were annealed at 120 °C for 16 h prior to removal from the glass substrate and evaporation of gold electrodes onto the sample for dielectric measurements.

Samples of pure PEO were compacted disks, 50.8 mm in diameter and about 3 mm in thickness. The disks were formed in a pellet press by compression of 5 g of the as-received PEO powder at 76.7 MP. Tin foil, 0.015 in. (J. T. Baker), electrodes were applied to the disks in accordance with ASTM D-150 specifications.[1]

Dielectric Measurements and Data Analysis. Dielectric measurements were carried out in the frequency range between 10^2 and 10^6 Hz using a combination of digital RLC bridges under computer control. The samples, in plane parallel capacitive geometry, were mounted on an isolated Cu plate in contact with a thermocouple and Pt resistance thermometers. The specimen holder was contained in a temperature chamber where the temperature (under computer control) could be maintained to a precision of 0.5 K over the temperature range of the measurements. Dielectric spectral data were taken from high to low and from low to high temperature without hysteresis in the peak positions. The sweep rate was typically 2 K/min. Dielectric spectra were deconvoluted into the minimum number of component peaks using commercially available software (Peak Fit, Jandel Scientific, Corte Madera, CA). The goodness of fit (correlation coefficient, R) was $R > 0.9995$. Peak asymmetry and Lorentzian character were used when the experimental curves could not be replicated by Gaussian component peaks. A primary criteria for acceptability of the component peaks was the agreement between the curve resulting from their summation and the original experimental curve.

Results

Dielectric Spectroscopy of PEO (3400 Da). As a control for our dielectric studies in PS/PEO composites, dielectric spectra at 10^3-10^6 Hz were obtained as a function of temperature for the low molecular weight homopoly(ethylene oxide) which we have used in our composites. Figure 1 shows characteristic plots of tan δ (ϵ''/ϵ') in the temperature range between 150 and 320 K which were obtained. The spectra show a single relaxation peak which narrows as the frequency decreases and whose maximum moves to higher temperature as the frequency is increased. The frequency dependence of the temperature at which the relaxation maximizes is characteristic of the well-documented β relaxation for the amorphous phase of PEO and is correlated with the previously reported glass transition temperature measurements for PEO.[2−4] Figure 2 shows

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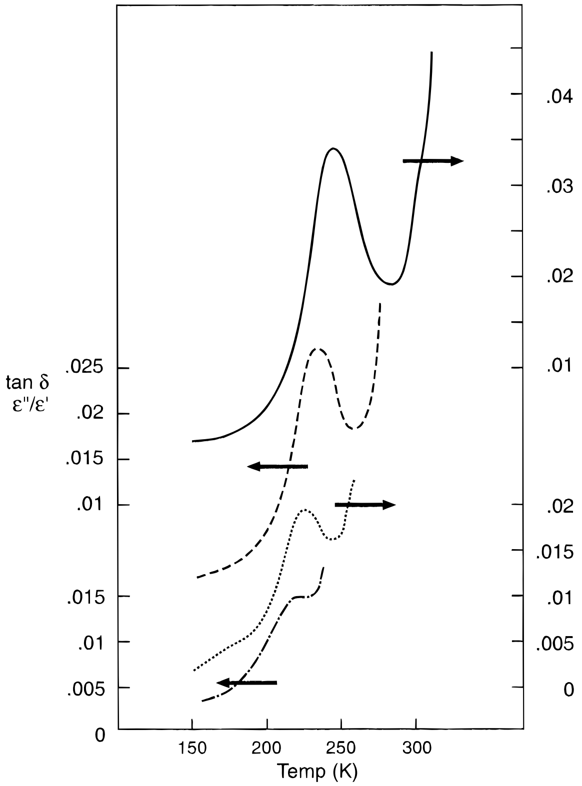

Figure 1. Temperature dependence of the dielectric spectrum, tan δ (ϵ''/ϵ') versus temperature, K, for PEO at 10^3 (- • -), 10^4 (• • •), 10^5 (— — —), and 10^6 (—) Hz.

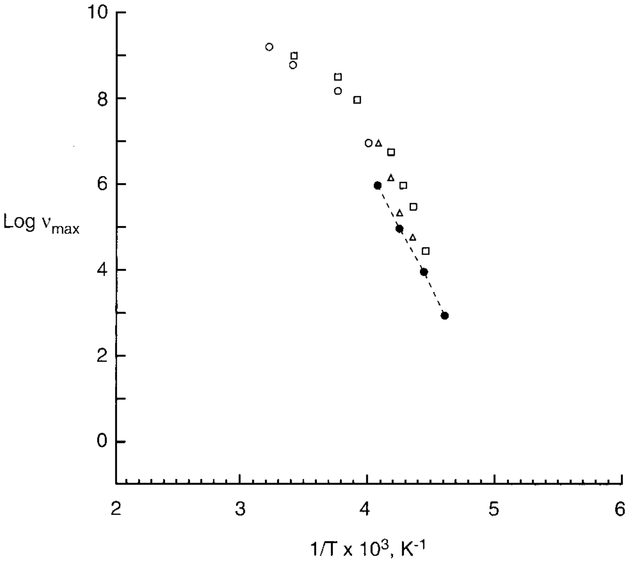

Figure 2. log ν_{max} versus $1/T$ (K) for 3 mm × 50.8 mm compacted disks of PEO(3400) (- ● -); data of Connor et al. for PEO samples of varying molecular weight (2.8×10^5 = ○, 2.8×10^6 = □, 8.4×10^5 = △).

a plot of log ν_{max} versus the reciprocal of the absolute temperature. The data which we have obtained correspond well with that reported by Connor et al., for PEO samples of varying molecular weight.

Dielectric Spectroscopy of PS/PEO Composites. PEO normally suffers large scale phase separation in blends with PS. However, a fairly uniform, micron-sized dispersion of PEO in PS can be obtained in films cast from cyclohexanone.[5] Figure 3 shows an optical micrograph of a typical 50 μm thick film [5% by weight of PEO (3400 Da) in PS] cast from cyclohexanone wherein one can see a uniform dispersion of 2−3 μm domains of PEO in a continuum of PS. Figure 4 displays dielectric spectra [tan δ (ϵ''/ϵ') versus absolute temperature] obtained from such a film. Depending on the frequency of the measurement, the spectra exhibit up to four well-defined relaxation peaks in the temperature range between 100 and 370 K. The base-line spectrum for the PS host at 10^3 Hz is also shown in this figure. Accordingly, it is assured that none of the relaxations in the PS/PEO composites is due to molecular relaxations in the PS host. The lowest temperature feature is a sub-T_g peak, well documented in the literature for PEO and identified as the γ relaxation.[3,4,6] At 10^6 Hz, the maximum of the γ peak occurs at 158 K. The breadth of this peak, *f*ull *w*idth at *h*alf-*m*aximum (fwhm), is about 104

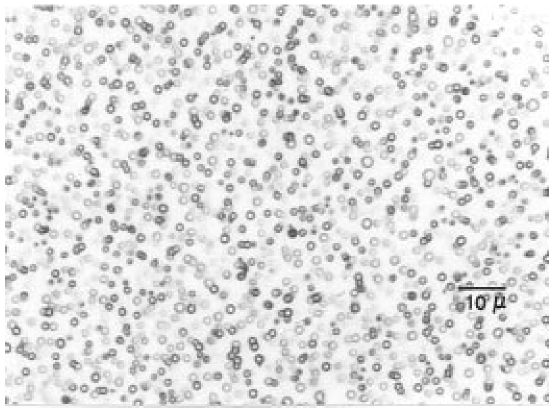

Figure 3. Optical micrograph of a ~50 μm thick film comprised of 5% by weight of PEO(3400) in PS. Magnification = 1024×, marker = 10 μm (reproduced at 60% of original size).

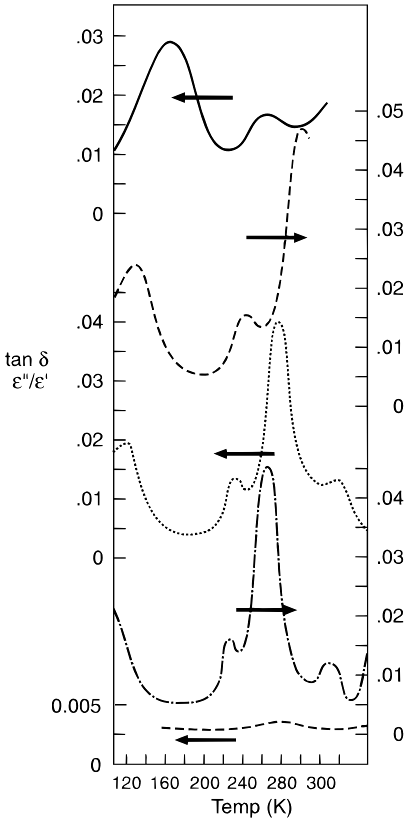

Figure 4. Temperature dependence of the dielectric spectrum, tan δ (ϵ''/ϵ') versus temperature, K, for a film comprised of 5% by weight of PEO(3400) in PS at 10^2 (- • - • -), 10^3 (• • •), 10^4 (— — —), and 10^6 (—) Hz. The dashed curve at the bottom of the figure denotes the dielectric spectrum of the PS host at 10^3 Hz.

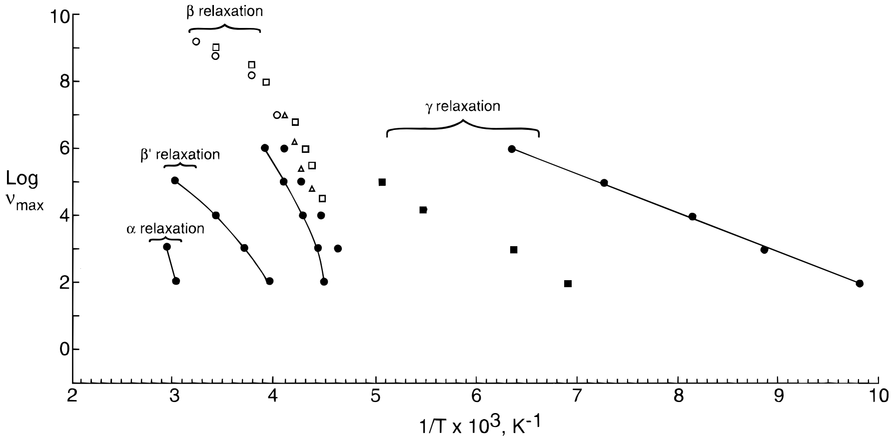

Figure 5. log ν_{max} versus $1/T$ (K) for ~50 μm thick film comprised of 5% by weight of PEO(3400) in PS (− ● −); PEO(3400) control, 3 mm × 50.8 mm compacted disks (●); data of Connor et al. for PEO samples of varying molecular weight (2.8×10^5 = ○, 2.8×10^6 = □, 8.4×10^5 = △, and 4×10^5 = ■).

K. The γ-peak maximum is progressively shifted to lower temperature as the frequency of the measurement is decreased; the peak width, fwhm, also decreases. At 10^3 Hz, the maximum in the γ peak occurs at 112 K and its fwhm is of the order of 40 K.

The β peak, which was also observed in PEO, is the second prominent feature of the dielectric spectra of PS/PEO composites. At 10^6 Hz, the maximum of the β peak occurs at 257 K. The fwhm of this peak is of the order of 34 K. The β peak also narrows, and its maximum shifts progressively to lower temperature as the frequency of the measurement is decreased. At 10^3 Hz, the maximum in the β peak occurs at 227 K and its fwhm is of the order of 21 K.

The two peaks occurring at temperatures in excess of the T_g have not previously been observed in the dielectric spectra of PEO. That occurring just above the β peak in temperature is the most dominant feature of the spectrum. Because of its proximity to the known β relaxation, this peak will be referred to as the β' peak. Like the γ and β peaks, the β' peak narrows and shifts to lower temperature as the frequency of the measurement is decreased. Because of this shifting, the maximum in the peak can no longer be observed in the 10^6 Hz spectrum. However, at 10^3 Hz the β' peak is positioned well within the 100−370 K temperature range.

The highest temperature feature is observable only in the 10^3 and 10^2 Hz spectra. At 10^3 Hz, this feature occurs at 320 K and shifts to 310 K at 10^2 Hz. Because of the correspondence of this relaxation with the crystalline melting temperature of PEO, this peak is assigned as the α relaxation.

Figure 5 shows plots of log ν_{max} versus the reciprocal of the absolute temperature (− ● −). These plots enable the analysis of the character of the relaxations and correlation with data from seminal studies of the dielectric properties of PEO. In order to facilitate this correlation, data reported by Connor et al.,[2] for PEO samples of varying molecular weight (2.8×10^5 = ○, 2.8×10^6 = □, 8.4×10^5 = △, and 4×10^5 = ■), are incorporated in Figure 5. Data for our control sample PEO (MW = 3400 Da) has also been included in this figure (●). Inspection of Figure 5 demonstrates that the γ peak is Arrhenius activated and corresponds to the reported γ relaxation.[3,4,6] The β and β' peaks are distinct. Both exhibit the curvature characteristic of a WLF[7] process. The α relaxation is readily distinguished from the β or β' process.

Discussion

The dielectric relaxation spectrum of PEO, as reported in the literature, exhibits only two broad peaks; the low-temperature γ peak (which has been attributed to localized motions in the crystalline chain segments) and the β peak (which is associated with the glass transition of PEO). The low-temperature γ peak appears at 100−200 K, depending on the molecular weight of the PEO and the frequency. The β relaxation appears at 220−315 K and is again dependent on the molecular weight of the PEO at each measurement frequency. The crystalline melting transition (α) in PEO has not previously been observed by dielectric measurements. The α transition is apparently obscured by losses associated with the highly conductive PEO melt.

The dispersion of PEO in an insulating continuum such as PS suppresses conductivity and allows the α peak to be elaborated. Pochan et al.[8] observed a high-temperature relaxation of the PEO segment of PS−PEO block copolymers which they termed the α_c and associated with the melt of PEO. Our dielectric observation of the of the α peak in homopoly(ethylene oxide) and its correlation with the PEO melt are, however, unequivocal.

The present observation of two dielectric β processes has no precedent. The high degree of correspondence between the β relaxation in the neat PEO control sample and that in the PS/PEO composite films is significant and enables its unequivocal assignment as the classic β relaxation associated with the glass transition of PEO (see Figure 5). We propose that the β' relaxation is associated with segmental motion of tethered PEO chain segments. In semicrystalline PEO phase, tethered segments would be those segments of amorphous PEO chains emanating from crystalline domains.

While a Maxwell−Wagner dispersion associated with the heterogeneous nature of the dielectric composite might, in principle, be expected (depending critically on the conductivity anisotropy and the geometry of micro-interfaces), none is in fact observed in the range of frequency and temperature which was accessed in the present work. In a related system, containing very large, salt-doped PEO domains of precisely controlled geometry and dimension, Hayward, Pethrick, and Siriwittayakorn[9] observed strong Maxwell−Wagner dispersions whose frequency dependence was in good agreement with the predictions of simple Maxwell−Wagner−Sillars theory. We are led to conclude that, in the

Table 1. Molecular Relaxations in PEO: Correlation of Dielectric Measurements with Published Dynamic Mechanical and Calorimetric Data[a]

relaxation	dielectric measurements[b] (this work)	calorimetric measurements Lang et al.[11]	mechanical measurements Boyer[10]
α	330	338−347	
β'	254	263−313	>205
β	223	190−240	170 ± 20
γ	102	130−140	

[a] Temperature, K. [b] Peak maxima at 100 Hz for samples comprised of 5% by weight of PEO(3400) dispersed as micron-sized domain in PS.

present system, the relatively low ionic conductivity and the microscopic dimensions of the PEO domains limit ion displacement and thus preclude the observation of inhomogeneous conductivity effects.

Boyer[10] has argued that semicrystalline polymers will exhibit two glass transitions, T_g(L) and T_g(U). He contends that T_g(U) arises from amorphous material under restraint by crystallites. Calorimetric studies by Lang et al.[11,12] have elucidated four relaxational transitions for PEO occurring at 130−140, 190-240, 263−313, and 338−347 K. The calorimetric data presented are the range of temperatures at which transitions were observed for samples of differing molecular weight. While they have not assigned them as we have, these calorimetric transitions correspond well with the γ, β, β', and α relaxations which we have observed dielectrically. Boyer correlated T_g(L) and T_g(U) in PEO with dynamic mechanical relaxations observed at 170 ± 20 and >205 K, respectively. Table 1 correlates the dielectric γ, β, β', and α relaxations identified in this work with the four calorimetric transitions for PEO observed by Lang et al.[11,12] and the dynamic mechanical β and β' relaxations identified by Boyer as T_g(L) and T_g(U).[10] Our dielectric assignments are the temperatures at which peak maxima occur in spectra taken at 100 Hz. In light of the differing molecular weight of the materials and the fact that we have not extrapolated dielectric data to limiting low frequency, correspondence with the calorimetric data of Lang et al. and the dynamic mechanical data of Boyer is quite good.

Summary and Conclusions

Our studies on PS/PEO composites have resulted in the observation of four molecular relaxation processes in PEO. They are the α relaxation associated with the crystalline melt of PEO;[2,3] two WLF type relaxations, β and β', which we speculate to be respectively associated with the onset of segmental motion and free-volume expansion of unrestricted amorphous PEO chains and with amorphous PEO chain segments tethered in crystallites; and a sub-T_g, γ relaxation associated with localized motions in the crystalline chain segments. In pure PEO, the α and β' relaxations are obscured by dc losses.

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