Anomalous Behavior in Blends of a Polychlorinated Biphenyl with Polystyrene Oligomer Investigated by Mechanical and Dielectric Spectroscopy

R. Casalini,[†,‡] P. G. Santangelo,[†] and C. M. Roland*,[†]

Chemistry Division, Code 6120, Naval Research Laboratory, Washington, D.C. 20375-5342, and
Chemistry Department, George Mason University, Fairfax, Virginia

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Dynamic mechanical and dielectric spectroscopy measurements on a polychlorinated biphenyl (PCB54), an oligomeric polystyrene (PS590), and their blend revealed various anomalies: (i) The mechanical relaxation times were always smaller (faster relaxation) than the relaxation times extracted from the dielectric modulus. (ii) The fragility (T_g-normalized temperature dependence of the relaxation times) for the two neat materials was the same, even though the shapes of the corresponding relaxation functions were quite different. Such a result is at odds with the well-established correlation between these quantities. (iii) The addition of PS590 speeds up dielectric relaxation of the PCB54, even though the former has a higher glass transition temperature. However, the mechanical response is normal; that is, the relaxation times of the mixture are intermediate between those of the pure components. A brief discussion of these anomalies is given.

Introduction

Dielectric and mechanical relaxation measurements are often used for investigation of the dynamics of glass formers. Because both the applied perturbation and the detected response may not be the same, different relaxation behaviors can be observed for the two spectroscopies.[1−4] Thus, a comparison of the two techniques can yield insights into the nature of the local motions. Herein we describe a case in which the mechanical and the dielectric measurements are different for two neat materials, as well as for their mixture. The two glass formers were chosen because their respective glass temperatures are nearly equal. This enables anomalies to be observed in the dynamics of their mixture. Moreover, the effect of blending is qualitatively different for mechanical as opposed to dielectric measurements.

Experimental Section

The polychlorinated biphenyl was Monsanto Aroclor 1254 (PCB54, obtained from J. Schrag of the University of Wisconsin), which is 54 wt % chlorine (primarily pentachlorobiphenyl). The oligomeric polystyrene (PS590, obtained from Polymer Scientific) had a molecular weight of 590, which corresponds to six monomer units per chain. The glass temperature for both PCB54 and PS590 was measured by DSC (at 10 deg/min) to be nearly the same, $T_g = 249 \pm 1$ and 247 ± 1 K, respectively. A blend having a concentration, $c = 0.12$ g of PS590/mL in Aroclor, was prepared by heating at ~320 K, accompanied by gentle mixing.

Dynamic mechanical measurements were obtained with a Bohlin VOR rheometer, using a parallel plate geometry. The complex dynamic shear modulus, $G^*(\omega)$, was measured over a frequency range of from 3×10^{-4} to 30 rad/s. Dielectric measurements were carried out using an IMASS time domain dielectric analyzer, an HP4284A LCR meter, and a Novocontrol Alpha analyzer. The use of three dielectric spectrometers provides a broad range: $6 \times 10^{-4} \leq \omega \leq 1 \times 10^7$ rad/s.

Temperature control for both mechanical and dielectric measurements was at least ±0.1 deg.
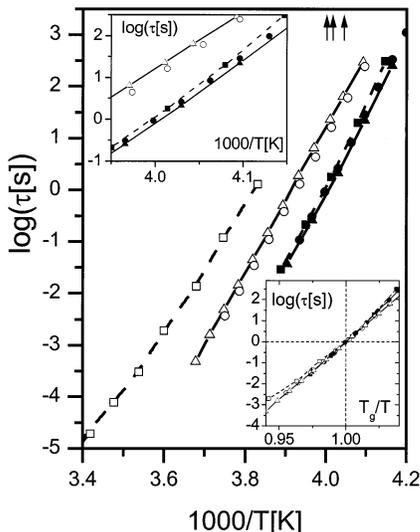
Results and Discussion

Dielectric relaxation times are commonly defined from the frequency of the maximum in the imaginary component of the dielectric dielectric permittivity, $\tau(\epsilon'') = 1/\omega_{max}$; however, these are actually retardation times. So, for consistency in making comparisons to relaxation times determined from the maximum in the mechanical loss modulus, $\tau(G'')$, we calculated the dielectric relaxation times as the maximum in the dielectric modulus, ($M^* = 1/\epsilon^*$).

As seen in Figure 1, the dielectric relaxation times, $\tau(M'')$, are significantly longer than the mechanical $\tau(G'')$, for both the PCB54 and the polymer. This implies that the dynamic glass temperature is *higher* when defined using the dielectric modulus than for the loss modulus. However, as seen in Table 1, the behavior is reversed if the comparison is made using retardation times, defined from the maximum in the corresponding permittivity and mechanical compliance, respectively. Because the difference between $\tau(M'')$ and $\tau(\epsilon'')$ depends on the dielectric strength, the relative magnitudes for the two spectroscopies vary for different materials.[5−10]

A useful approach to assess the dynamics of glass formers is by comparison of their T_g-normalized temperature dependences. The steepness of such T_g-scaled Arrhenius plots ("fragility") provides a means to classify the behavior of different glass formers.[11−13] In the lower inset to Figure 1, we show such a plot for both the mechanical and dielectric data of the two neat materials, using a T_g defined as the temperature at which $\tau(G'')$ and $\tau(M'') = 1$ s. (The particular time is arbitrary, and this choice avoids having to deconvolute from the dielectric spectra the dc conductivity, which contributes strongly at lower frequencies, due to the weak dielectric strength of polystyrene.) It is evident that the four curves are essentially the same, indicating that not only do the two spectroscopies give equivalent results, but moreover, the fragilities of PS590 and PCB54 are very close. We can quantify this from the slope at T_g, obtaining $m \equiv$ d log(τ)/ d$(T/T_g)|_{T=T_g} = 57 \pm 3$.

† Naval Research Laboratory.
‡ George Mason University.

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Figure 1. Mechanical (solid symbols) and dielectric (open symbols) relaxation times for PCB54 (triangles), PS590 (squares), and their mixture (circles) ($c = 0.12$ g/mL). The top inset shows a partial enlargement, revealing in more detail the behavior. The arrows in the main figure shows the respective T_g as determined from DSC for (from right to left) PS590 ($T_g = 247$ K), PCB54 ($T_g = 249$ K), and their blend ($T_g = 250$ K). The lower inset shows the relaxation times for the neat materials after normalizing the temperature variable by T_g, defined as the temperature at which $\tau = 1$ s. Symbols in the insets are the same that in the main figure.

TABLE 1: Dynamic Glass Temperatures from Spectroscopy Data

| | T_g ($\tau = 1$ s) (K) | | | |
	$G''(\omega)$	$M''(\omega)$	$J''(\omega)$	$\epsilon''(\omega)$
PCB54	249.5	255.6	>257[a]	256.0
PS590	250.2	261.8	↓	261.8
blend	249.9	254.6	↓	255.3

[a] The maxima in the mechanical loss compliance fall at frequencies lower than the measurement range.

Because the fragility is expected to correlate with the breadth of the α-relaxation function at $T \sim T_g$,[14-16] we expect the respective shapes of the PCB54 and PS590 dispersions to be very similar, and independent of the method of measurement. As seen in Figures 2 and 3, for either material, we find that the mechanical and dielectric measurements are indeed very similar. We can fit the $G''(\omega)$ spectra to the Laplace transform of the Kohlrausch−Williams−Watts (KWW) function[17,18]
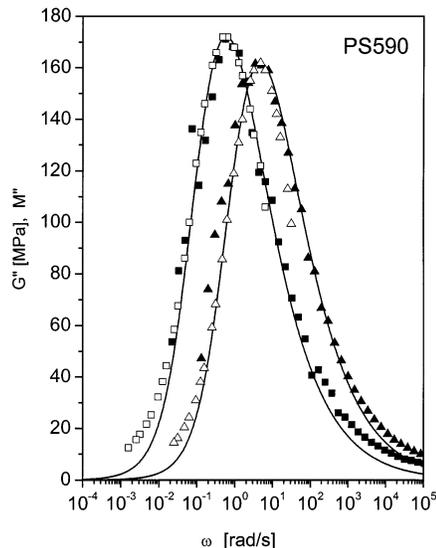
$$G''(\omega) = \omega G_0 \int_0^\infty \exp[-(t/\tau_G)^{\beta_G}] \cos(\omega t)\, dt \qquad (1)$$
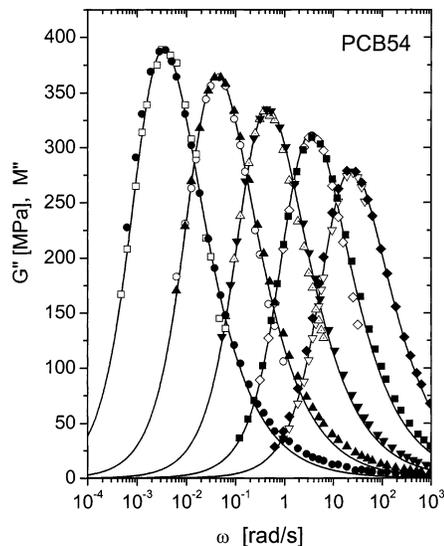
and similarly for the dielectric modulus

$$M''(\omega) = \omega \Delta M \int_0^\infty \exp[-(t/\tau_M)^{\beta_M}] \cos(\omega t)\, dt \qquad (2)$$

where G_0 is the unrelaxed modulus, ΔM is related to the dielectric strength, τ_G and τ_M are the KWW relaxation times, and β_G and β_M are the stretch exponents. The stretch exponent defines the degree of nonexponentiality of the relaxation function in the time domain, or equivalently the breadth of the dispersion in the frequency domain.

Near T_g, we find $\beta_G = \beta_M = 0.44$ for PS590, and $=0.62$ for PCB54. The greater breadth measured for the polystyrene is an interesting result, because it implies a breakdown of the expected correlation between the peak breadth and fragility. Comparing these values with results obtained on many other glass formers,

Figure 2. Comparison of mechanical and dielectric spectra for PS590. The solid symbols are the dielectric loss modulus, and the open symbols the mechanical loss modulus (the latter at $T = 249$ K (□) and $T = 253$ K (△), respectively). The dielectric spectra were normalized to the maximum of the mechanical data and slightly shifted to superpose the maxima. The solid lines represent the Laplace transform of the KWW functions (eq 1 and 2) with $\beta_M = \beta_G = 0.44$.

Figure 3. Comparison of the mechanical loss modulus (open symbols) with the imaginary part of the dielectric modulus (solid symbols), for PCB54. The temperatures of the G'' spectra are 240 K (○), 244 K (△), 248 K (◇), 252 K (▽), and 256 K (□). The dielectric spectra having peak frequencies closest to $1/\tau(G'')$ were chosen for the comparison. They were shifted slightly in frequency and vertically scaled to coincide with the loss modulus. The solid lines present the Laplace transform of KWW functions (eq 1 and 2) with $\beta_M = \beta_G = 0.62$ (three lowest frequency spectra) and $\beta_M = \beta_G = 0.63$ (two higher frequency spectra).

describable by the approximate relationship $m = 250(\pm30) - 320\beta$,[15] the behavior of the PS590 is seen to be exceptional; that is, it is broader than expected from its value of m.[19] A related anomaly has been observed previously for polystyrene; to wit, there is a systematic increase in fragility with increasing molecular weight, even though the shape of the segmental relaxation dispersion is invariant to molecular weight.[20] An interpretation of this phenomenon in terms of the contribution of chain end groups has been suggested.[21,22]

In a previous paper,[23] dielectric and mechanical measurements on PCB54 blended with a high molecular weight PS ($M_w = 90$

$\times 10^3$) were reported. In that case, notwithstanding a difference of 130 deg between the T_g of the two materials, addition of the high molecular weight polystyrene had an almost negligible effect on the dielectric relaxation times of PCB54. On the other hand, the mechanical relaxation times exhibited the expected large increase upon addition of the PS.

In the present paper, we examine the effect of addition of oligomeric PS to the PCB54, these components having the same calorimetric T_g. As seen in Figure 1 (open symbols), the mechanical spectroscopy results are as expected, $\tau(G'')$ for the blend being intermediate between the relaxation times of the two neat components. However, the dielectric measurements (solid symbols in Figure 1) are counter intuitive: $\tau(M'')$ for the blend is smaller than the relaxation times of either neat component. The addition of the PS590 causes anomalous plasticization of the A1245.

These results are summarized in Table 1, which displays the dynamic glass temperatures, $\tau(T_g) = 1$ s, for both pure components and the mixture. Note that this anomaly is seen in both the dielectric modulus and the permittivity representations of the data, each τ corresponding to the reciprocal of the frequency of the maximum of the respective dispersion. For the loss compliance, however, the peak falls outside of the range of our measurements. We can quantify this modification of the PCB54 dynamics by calculating the change in the effective friction coefficient, defined as $\xi(T) = \tau(c,T)/\tau(0,T)$, where $c = 0$ refers to the neat PCB54. From mechanical spectroscopy, we obtain $\partial \ln \xi(T_g)/\partial c = 0.20$ mL/g. The dielectric measurements yield an opposite result, $\partial \ln \xi(T_g)/\partial c = -0.32$ mL/g.

A similar anomalous plasticization was previously seen in an Aroclor (Aroclor 1248, having a lower chlorine content) blended with 1,2-polybutadiene.[24−26] In that case, the origin of the plasticization was ascribed to a positive excess volume. Obviously, a change in volume upon mixing cannot account for the qualitatively different behavior observed in the present case by different spectroscopies.

A possible explanation may be found in the dynamical behavior of neat PS590, in particular the large difference observed between $\tau(M'')$ and $\tau(G'')$. The dielectric measurements on the blend reflect primarily the contribution of the PCB54, because it has a dielectric strength that is ~60 times larger than for the PS590. This causes the dielectric results for the blend to weight primarily the Aroclor component, consistent with Figure 1. However, it cannot account for the negative sign of the $\partial \ln \xi(T_g)/\partial c$ determined from dielectric measurements.

The fact that the mechanical relaxation times are *shorter* than the corresponding $\tau(M'')$ suggests that alleviation of stress is governed by the more mobile molecular segments. For PS590, this involves the chain ends. This is consistent with the experimental finding that the fragility of PS varies inversely with molecular weight,[20] also an effect due to chain ends.[22] We also point out that in a previous comparison of the component dynamics in polymer blends,[27,28] the mechanical response was found to track predominantly the faster relaxing component. It is tempting to conclude from such results that local relaxation of stress in polymers involves a "series coupling" of the relaxing segments; to wit, $\tau \sim (\sum 1/\tau_i)^{-1}$ (additivity of the strains rather than of the stresses[29,30]). This naïve suggestion is meant to do no more than stimulate further analysis.

Conclusions

Mechanical and dielectric spectroscopies were carried out on PCB54 and PS590, two glass-forming liquids with nearly identical glass temperatures. Several anomalies were observed in the dynamics of both the neat materials and their blend. The mechanical relaxation times were always shorter (faster relaxation) than the dielectric relaxation times. However, except for the neat polystyrene (for which the maximum in the loss compliance was not measured), this ranking was reversed when the comparison was made using the retardation times. The fragility was equivalent for the two neat materials, notwithstanding differences in the shape of their respective relaxation functions. This is contrary to the expected correlation between the breadth of the relaxation function and the nonexponentiality of the relaxation times.

A mixture of PS590 and PCB54 was found to relax faster, as measured dielectrically, than either neat component. This result is unusual, because the properties of mixtures are generally expected to fall intermediate between the pure component properties. When measured mechanically, however, the behavior was normal.

Although presently a satisfactory explanation of these phenomena is lacking, a more detailed examination of the relative contribution of the chain ends and midpoints to the dynamics of polymer molecules will prove fruitful. This will likely require labeling and alternative experimental measurements, such as NMR or infrared spectroscopy.

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