# Segmental Relaxation in Blends of Polychloroprene and Epoxidized Polyisoprene

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**ABSTRACT:** Dynamic mechanical measurements were conducted over a range of frequencies in the glass transition zone of an epoxidized (25 mol %) polyisoprene (EPI), polychloroprene, and miscible mixtures thereof. The neat polymers had nearly equal glass transition temperatures. Furthermore, they were found to exhibit very similar segmental dynamics, including their segmental relaxation times, functions, and temperature dependencies. Interestingly, however, blends containing a relatively high concentration of the EPI had shorter relaxation times (by up to an order of magnitude) than the neat components; that is, segmental relaxation speeds up upon mixing. This behavior is interpreted in terms of the decrease in intermolecular cooperativity in the mixtures relative to the neat components. The decrease is associated with a large positive excess volume of mixing measured for the blends and the consequent increased unoccupied volume.

## Introduction

Much of the segmental relaxation data found in the literature are interpreted in terms of free volume ideas. This is done by explicit application of free volume-based theories such as those of Bueche[1] and Fujita[2] or implicitly, for example through use of the WLF equation.[3] Since relaxation associated with the glass transition involves the rearrangement of segment volumes substantially larger than the largest vacancies,[4–7] it is considered that the average free volume, not its distribution, governs the glass transition.[3,8]

Arguments have been advanced against the interpretation of polymer dynamics in terms of a static quantity such as free volume (see, for example, refs 9 and 10). Molecular motion in the bulk state is inherently cooperative and although free volume exerts an influence on relaxation, it can successfully describe relaxation in complex systems only when intermolecular cooperativity is accounted for.

A qualitative inference drawn from free volume theories is the expectation that the glass transition temperature ($T_g$) and relaxation times of miscible mixtures will be intermediate to those of the pure components. This is usually observed, at least when the components have very different glass transition temperatures. However, dielectric[11] and dynamic mechanical measurements[12] have demonstrated that the addition of poly(vinylethylene) (PVE) speeds up the reorientation dynamics of polychlorinated biphenyl (PCB), even though the polymer has a $T_g$ 30 deg higher than that of the PCB. Similarly, the introduction of a small quantity of higher $T_g$ poly(methylphenylsiloxane) (PMPS) reduces the reorientational relaxation time of 1,1-bis(*p*-methoxyphenyl)-cyclohexane (BMC).[13] Addition of lower molecular weight PMPS, having the same $T_g$ as BMC, also results in increased mobility of probe molecules diffusing in the BMC.[14]

While in these two systems, PVE/PCB and PMPS/BMC, there is an unexpected increase of the relaxation rate upon mixing, the converse anomaly has also been observed. At the appropriate molecular weights, poly(epichlorohydrin) and poly(vinyl methyl ether) have equivalent glass transition temperatures; nevertheless, the segmental relaxation times of the mixtures, measured dielectrically, are longer than that of either component.[15]

These results, wherein mixtures exhibit relaxation times and glass transition temperatures that are not intermediate to those of the components, have been ascribed to two factors—constraint dynamics and nonzero excess volumes. The first explanation, based on the coupling model,[16,17] considers the contribution to the observed relaxation times from intermolecular constraints. Since these constraints, or crowding couplings, can change upon blending, their influence on the relaxation dynamics is not obvious from the behavior of the neat components. For example, neat PMPS is associated with stronger intermolecular coupling than neat BMC, as determined from the shape of their respective segmental relaxation functions.[13] This stronger coupling, while raising the $T_g$ of neat PMPS, is irrelevant to the effect of adding a small amount of the polymer to BMC. The relaxation of BMC speeds up, since it experiences a smaller local friction coefficient in the presence of added PMPS.[13]

A similar explanation has been proposed for the anomalous speeding up of PCB in the presence of PVE.[11] However, an experimentally observed positive excess mixing volume for that mixture contributes to, and may in fact govern, the relaxation dynamics.[12] In general, additivity of the volumes is not expected (e.g., refs 18 and 19). For miscible polymer mixtures, where there is intimate contact between the component polymers, densification has generally been expected and, although studies of the volume changes on mixing two polymers are relatively rare, has been observed experimentally in a number of cases.[20,21] Densification reduces the unoccupied volume, presumably slowing down the relaxation. The opposite effect has been shown to be operative in the PCB/PVE mixtures and is responsible, at least in part, for their anomalous relaxation behavior.[12]

Although constraint dynamics and its composition dependence, as well any changes in free volume accompanying mixing, are both anticipated to influence the relaxation behavior of blends, manifestations of these phenomena can only be directly discerned when the glass transition temperatures of the components are close. In this circumstance qualitative deviations from conventional

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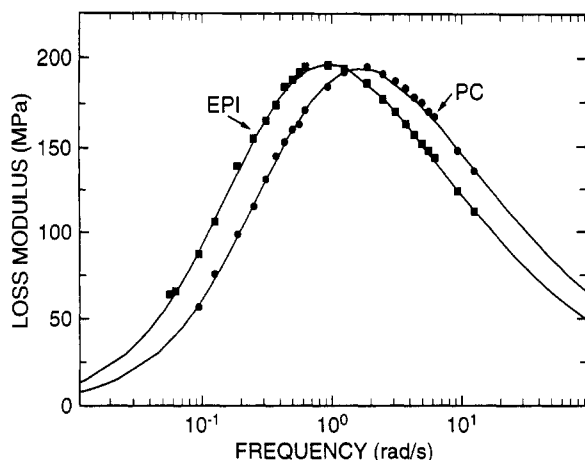
**Figure 1.** Mechanical loss modulus spectra for the neat polymers at −39 °C, along with the best fit curves calculated using eqs 1 and 2. The peak frequencies differ by less than a factor of 2, which corresponds to a temperature change of less than 1 deg.

expectations can be seen. More usually the components' $T_g$'s are very different, so that any consequences of these factors are not readily apparent. A full quantitative theory of mixture dynamics is required; however, such a development is remote, given the complexity of cooperative dynamics even in neat liquids and polymers.

In the present study we have investigated the dynamic mechanical behavior of blends of polychloroprene (PC) and epoxidized polyisoprene (EPI). When the epoxidation level of the latter is 25%, these polymers have nearly equal glass transition temperatures. Although this precludes the use of most conventional methods of assessing miscibility, thermodynamic miscibility in this system has been demonstrated by $^{129}$Xe NMR spectroscopy.[22] The miscibility has been ascribed to a relatively weak interaction between the oxirane group on the EPI and the Cl atom of PC.[23,24]

### Experimental Section

The polymers were gel-free portions of a 25 mol % epoxidized natural rubber (Epoxyprene 25, a random copolymer of 2,3-epoxy-2-methylbutane and 2-methyl-2-butene from Guthrie Latex, Inc., Tucson, AZ) and polychloroprene (primarily *trans*-poly(1-chloro-1-butenylene), WM-1 Neoprene from DuPont Co., Wilmington, DE). Blends containing 10, 30, 50, 70, and 90 wt % EPI were prepared from 2% THF solutions, followed by vacuum drying.

Room temperature specific gravities relative to methanol were measured using the buoyancy method (ASTM method D792 A-1). Typically, three samples of each blend and of the neat polymers were measured. A Mettler MT5 balance (accuracy = $10^{-6}$ g) was used, with sample masses exceeding 0.1 g.

Dynamic mechanical data in the transition zone were obtained with a Bohlin VOR rheometer. A parallel plate geometry was used, with sample diameters of 6.25 mm and typically a 3.5 mm gap. Initially, samples were annealed in the instrument for ca. 30 min at 50 °C to ensure good contact with the plates and to eliminate any crystallinity in the PC. The shear modulus was measured at a series of frequencies in the range of ca. 10 to $10^{-4}$ Hz at temperatures from −37 to −45 °C. Temperature control was maintained to ±0.1 deg.

### Results and Discussion

**A. Neat Polymers.** Displayed in Figure 1 is the measured relaxation dispersion in the $T_g$ region for neat EPI and PC. The data are fitted to the well-known Kohlrausch−Williams−Watts (KWW) stretched exponential function[25,26]

$$G(t) = G_0 \exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right] \quad (1)$$

using

$$G''(\omega) = \omega \int_0^\infty G(t) \cos(\omega t)\, dt \quad (2)$$

where $G_0$ is a constant, $\tau^*$ is the segmental relaxation time, and $0 \leq n \leq 1$. Although originally an empirical fitting function, eq 1 can be derived[16] by introducing the quantity $(t/t_c)^{-n}$ into the Hall−Helfand function[27] describing segmental relaxation of chains in the absence of intermolecular coupling. The factor $(t/t_c)^{-n}$ accounts for the slowing down of the relaxation due to constraints from nonbonded neighboring chains. The coupling parameter, $n$, therefore provides a measure of the extent of intermolecular coupling—a broader (more nonexponential) relaxation function is associated with stronger coupling. Recent quasi-elastic neutron scattering experiments,[28] as well as molecular dynamics simulations,[29] have confirmed the existence of a temperature-independent crossover time, $t_c$, at which segmental relaxation assumes the KWW form.

It can be seen in Figure 1 that the dispersions for the two neat polymers have very similar breadths, corresponding to $n \sim 0.51$. This equivalence implies that their relaxations are constrained to a similar degree by intermolecular cooperativity. From the fitting of the dispersions obtained at all measurement temperatures, it was found that, as usual, the magnitude of the coupling parameter varied only very weakly with temperature. In Figure 2 the relaxation times are plotted as a function of temperature, demonstrating that both the relaxation times and temperature dependencies are similar for the two polymers. This result is in fact an extant prediction of the coupling model. The relaxation time is related to the coupling parameter according to[17]

$$\tau^* = [(1-n)\omega_c^n \tau_0]^{1/(1-n)} \quad (3)$$

The noncooperative (primitive) relaxation time, $\tau_0$, prevailing at short times ($t < t_c$) before torques and unbalanced forces from neighboring segments begin to retard the relaxation, can be identified with one of the Hall−Helfand (intramolecularly correlated) relaxation times.[16] The value of $\tau_0$ is mainly governed by the spectrum of skeletal bond conformational transition modes.[27,30] Assuming that the temperature dependence of $\tau_0$ is similar for two polymers, eq 3 reveals that the observed temperature dependence (i.e., that of $\tau^*$) will scale in accord with the magnitude of $n$. This correlation of time and temperature dependencies has been verified for a large number of polymers[31–35] and small-molecule glass formers.[36–39] Since the segmental relaxation dispersion of EPI and PC have equal breadths (i.e., the same $n$), the equivalence of their temperature dependencies seen in Figure 2 is expected.

**B. Blends.** Since the segmental dynamics of the component polymers are quite similar, it is of interest to investigate mixtures of EPI and PC, previously shown to be thermodynamically miscible.[22,23] It is known that when the components have very different glass transition temperatures or relaxation functions (i.e., coupling parameters), a blend may exhibit an unusually broad relaxation spectra,[40,41] along with an absence of thermorheological simplicity.[33,41–43] Indeed, in such dynamically heterogeneous mixtures, the components can have measurably different mobilities and relaxation times
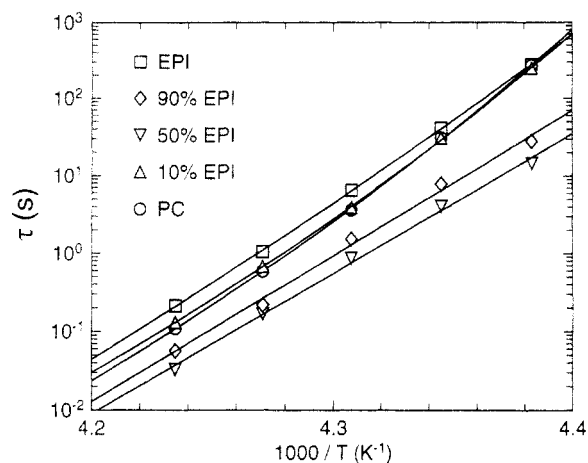
**Figure 2.** Temperature dependence of the segmental relaxation times for EPI, PC, and three blends. When enriched with EPI, the latter exhibit faster relaxation than the neat components. The solid curves represent the fit of the Vogel function (eq 4) to the data, whose interpolation to $\tau^* = 100$ s yields a value for the glass transition temperature.

**Table 1. Glass Transition Temperatures**

|        | $T_g$ (K)[a] | $T_g$ (K)[b] |
|--------|---------|---------|
| EPI    | 228.5   | 229.2   |
| PC     | 231.4   | 229.0   |
| 10% EPI |        | 229.0   |
| 50% EPI |        | 226.0   |
| 90% EPI |        | 226.8   |

[a] Differential scanning calorimetry at 20 K min$^{-1}$. [b] Temperature at which segmental relaxation time equals 100 s.

within the same composition.[44] The present system represents the opposite situation—the neat components have comparable segmental dynamics.

The segmental relaxation times measured for three blend compositions are shown in Figure 2. The relaxation times for the 10% EPI blend are seen to be very similar to those of the PC. The striking feature of the data is that blends containing 50 and 90% EPI exhibit shorter relaxation times than either of the neat components. The addition of 10% PC to EPI reduces the measured relaxation time by up to an order of magnitude. This anomaly, wherein the blend dynamics are faster than those of either of the neat components, is reminiscent of the behavior of the PCB/PVE[11,12] and BMC/PMPS[13] mixtures, in which the addition of a higher $T_g$ polymer effected reduction of the relaxation time. Also included in Figure 2 are the best fits to the Vogel equation:[3]

$$\tau^* = A \exp\left(\frac{B}{T - T_\infty}\right) \quad (4)$$

whose interpolation to a relaxation time of 100 s yields an operational value of the glass transition temperature. $T_g$ defined in this way was found to vary from about 229 K for PC, EPI, and the 10% EPI blend to ~226 K for the 50% EPI blend. These values are listed in Table 1, along with the calorimetric glass transition temperatures measured for the pure components.

As discussed above, the earlier results on PCB/PVE and BMC/PMPS mixtures were interpreted in terms of two effects—intermolecular cooperativity and nonzero mixing volumes. Notwithstanding the similarity in relaxation behavior of the two pure species, the strength of the intermolecular coupling, which governs the observed $\tau^*$ (eq 3), and its dependence on chemical structure[32,35,45] may change upon blending. Stronger coupling in the blend, conceivably occasioned by specific interactions between
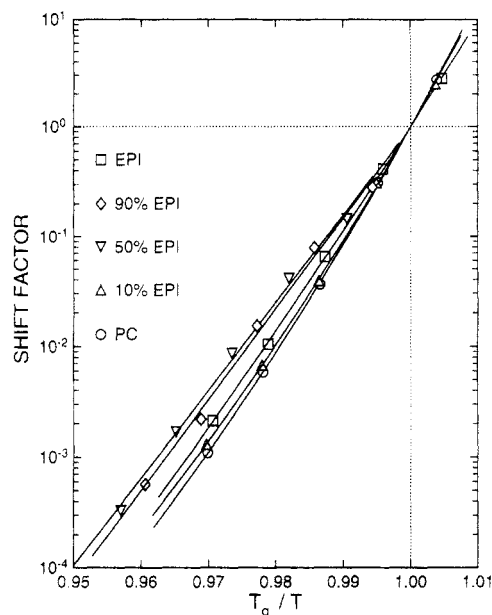


**Figure 3.** Segmental relaxation times for the neat polymers and blends displayed as a function of the reciprocal of the $T_g$-normalized temperature. The suggestion of these cooperativity plots is that there are weaker intermolecular constraints on the segmental motion in the blends containing 50 and 90% EPI.

the components, would be expected to increase $n$ and hence $\tau^*$. A relaxation time for a miscible blend longer than either pure component has recently been reported.[15] This situation is not expected herein, however, given the relative weakness of the chemical interactions between PC and EPI.[23]

The smaller $\tau^*$ of the blends could arise from weakened intermolecular cooperativity, which for a homogeneously broadened relaxation would be associated with a smaller value of $n$. Although the breadth of the $G''$ dispersion is marginally greater for the 90% EPI blend than that of the pure components, this cannot be directly interpreted in terms of the strength of the intermolecular coupling. The distribution of local environments in a miscible mixture resulting from concentration fluctuations can contribute to the measured relaxation function, making problematic the determination of $n$ by fitting the observed dispersion. In other words, interpretation of the shape of the relaxation function in terms of the coupling scheme, such as by fitting to eq 1, is strictly applicable only for homogeneous materials.

It has been shown, however, that when the measured relaxation is inhomogeneously broadened, for example due to crystallinity or cross-linking, the degree of intermolecular cooperativity can still be assessed from the temperature dependence of the relaxation time.[46] For example, experimentally observed temperature dependencies are frequently non-Arrhenius; consequently, some normalization scheme must be employed to compare the effect of temperature on the relaxation times. A plot of the relaxation time versus $T_g$-scaled temperature is now a well-established method for comparing temperature dependencies.[34,36,37,47]

In Figure 3 semilogarithmic depictions of $\tau^*$ versus $T_g/T$ ("cooperativity plots") are displayed for the neat polymers and blends. As noted previously, the glass transition temperatures have been operationally defined as the temperature at which the relaxation time equals 100 s, using the Vogel fits (eq 4) to interpolate the data points. While the neat polymers have cooperativity plots that are essentially equal, the data in Figure 3 indicate that the blends containing a substantial concentration of the EPI
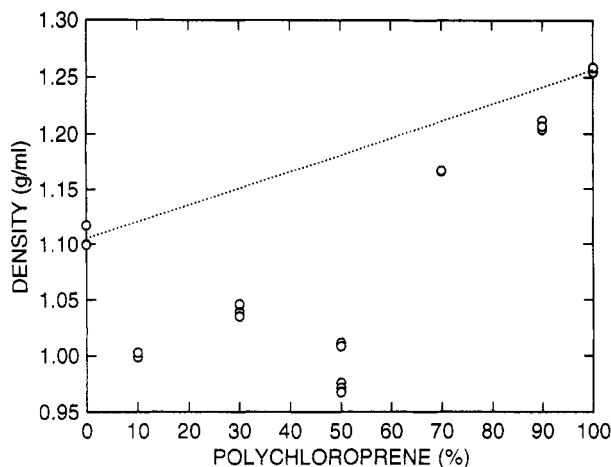
**Figure 4.** Composition dependence of the mass density for EPI, PC, and their blends. The points correspond to individual measurements, many of which overlap. The line represents the arithmetic average of the pure component densities. A marked decrease in density occurs, particularly for those mixtures exhibiting faster relaxation than the neat polymers.

exhibit a somewhat weaker dependence of $\tau^*$ on temperature. This implies weaker intermolecular coupling, and it is tempting to infer that this is the origin of the shorter relaxation times seen for the EPI-rich mixtures.

As noted, the other factor with the potential for influencing segmental relaxation times in the blends is any excess volume associated with mixing. Nonadditivity of the volumes could contribute to changes in the relaxation times.[2,48] To gauge this contribution in the blends, the specific gravities of the pure components and the blends were measured (Figure 4). It is interesting to note that the densities of blends containing 50% or more EPI not only are less than the arithmetic average of the component densities but, in fact, are actually less than that of either neat component. The largest excess mixing volumes are observed at high EPI concentrations (e.g., as much as ~15% for the 50% blend).

Relatively modest density decreases (<1%) due to mixing have been observed previously in a number of polymer–solvent systems,[49-51] and this has been qualitatively explained by arguments based on the equation of state theory of polymer solutions. For miscible polymer blends, where there is intimate contact between the component polymers, densification has generally been the rule. Although few studies of excess volumes of mixing for polymer blends have been reported, density increases on mixing have been observed in a number of cases (e.g., refs 20 and 21). However, for blends of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA), which are well known to be miscible in the melt, Wendorff et al.[52,53] reported a small (0.2%) positive excess mixing volume. It was postulated that this behavior results from the relatively strong interactions between PVDF and PMMA.[53,54] This is unlikely to be the origin of the behavior in the present case since the intermolecular interactions are relatively weak.[23] More recently, positive excess volumes (<1%) have been measured for a number of blends which exhibit hydrogen-bonding interactions.[55] The authors rationalized this behavior by considering the effect of chemical structure on chain packing.

The origin of the very large excess volumes of mixing seen herein for the EPI/PC blends is unclear and currently under investigation. Notwithstanding the unusual magnitude of the apparent decrease in density, the negative deviation from the arithmetic average of the pure components' densities is sufficient to qualitatively explain the

data in Figure 2. From free volume considerations, an increase in unoccupied volume would speed up the relaxation compared to that of the component polymers, consistent with the experimental results. This interpretation is supported by the observation that the EPI-rich mixtures, which are those exhibiting the most anomalous relaxation behavior, also exhibit the largest decrease in density.

## Summary

As illustrated by the results herein, deviations from conventional behavior can be observed through the study of mixtures whose components have nearly equal $T_g$'s. The anomalous segmental dynamics of the EPI/PC blends can be interpreted in terms of intermolecular cooperativity and its relationship to occupied volume. An increase in unoccupied volume alleviates intermolecular constraints on the segmental dynamics, thus increasing the relaxation rate. The weaker intermolecular cooperativity in the blends as revealed by the cooperativity plots (Figure 3) is likely a direct consequence of the positive excess volume.

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