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# Concentration fluctuations and dynamic heterogeneity in PIP/PVE blends

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## Abstract

Usually the shape of the glass transition dispersion in the mechanical or dielectric spectra of pure polymers is skewed toward higher frequencies. In miscible polymer blends not only is this peak broader than in pure polymers, the broadening is often asymmetric towards lower frequencies. Concentration fluctuations are an obvious source of the broadening; however, a simple distribution of relaxation times, corresponding to a distribution in local compositions, would not account for the reversal in the asymmetry of the dispersion. Intrinsic differences in component mobilities, as directly seen in solid state nuclear magnetic resonance experiments, also exert an influence on segmental relaxation in blends. The differences in the components' segmental relaxation behaviors are also manifested in the thermorheological complexity of miscible blends. An approach to blend dynamics based on the coupling model of relaxation can successfully describe the most prominent features.

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## 1. Introduction

The segmental relaxation behavior of a polymer blend usually differs significantly from that of the components. In some cases behavior not realizable with neat materials is exhibited, an example of which is the breakdown of time-temperature superpositioning in both the segmental [1,2] and the terminal [3,4] zones of the viscoelastic spectrum. The segmental relaxation dispersion for blends is usually broader than that of the pure components. Particularly striking is the reversal [1,5-7] of the characteristic asymmetry towards higher frequency

associated with segmental dispersion of pure amorphous polymers. In some blends a very marked low-frequency tail develops as the measurement temperature is lowered.

For blends one obvious source of the broadening of the relaxation spectra in the glass transition region is concentration fluctuations [8-11]. The local composition within a blend fluctuates about its average value, whereby chain segments experience differing local environments, giving rise to inhomogeneous broadening of the relaxation.

Another broadening mechanism operative in blends is from intrinsic differences in the relaxation properties of the components. In this note we discuss the consequences of this on the segmental relaxation behavior of PVE/PIP blends.

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## 2. Dynamic heterogeneity

Differences between the components' chain diffusion constants and terminal relaxation times have been reported for a number of miscible blends, including polystyrene/poly(2,6-dimethyl 1,4-phenylene oxide) [12], poly(ethylene oxide) and poly(methacrylate) [3], polybutadienes of differing microstructure [4], as well as PVE and PIP [4,13]. These results are generally interpreted in terms of differences in the local friction factor for the components and their respective degrees of entanglement [3,4,13,14]. This dynamic heterogeneity is well established in polymer-diluent mixtures [15–18].

The first direct evidence for differences in local chain dynamics between the components of a miscible polymer blend came from solid state  $^{13}\text{C}$  magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy on PIP/PVE blends [19]. The blend is of interest in this regard because of the unusually broad loss peak in the dynamic mechanical spectrum. At 75% PVE composition, the segmental dispersion is extraordinarily broad, encompassing that of the pure components [2]. In Fig. 1 the loss modulus is shown for the blend with 25% and 75% PVE. A high concentration of

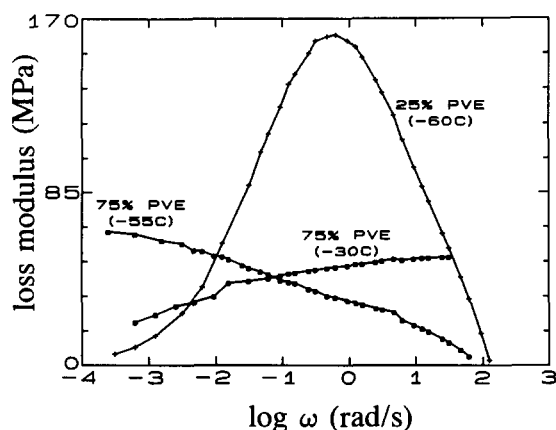


Fig. 1. Dynamic mechanical loss modulus measured in the vicinity of the glass transition temperature for blends of PIP with 25% PVE and 75% PVE, respectively. The breadth of the peak for the PVE-rich composition extends beyond the range of experimental frequencies available; hence, results are shown for two temperatures.

PVE is associated with extreme broadening. This breadth, along with the thermorheological complexity of miscible blends [1,2], makes it difficult to obtain the shape of the peak with conventional mechanical spectrometers (which typically access only a few decades of frequency).

The solid state  $^{13}\text{C}$  MAS-NMR technique allows the components of a blend to be differentiated by their isotropic chemical shifts. As shown in Fig. 2 (the  $^{13}\text{C}$  spectrum for a blend of 32% PIP and 68% PVE), both polymers have two resolvable peaks in the vinyl region of the spectrum. Local motions of the polymers affect the efficiency with which magic angle spinning averages the  $^{13}\text{C}$  chemical shift anisotropy (CSA). When this motion is on the same timescale as the MAS (3 kHz for the spectra in

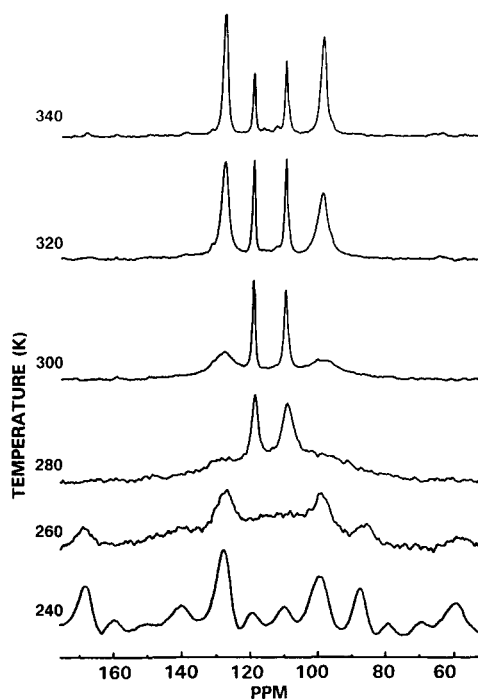


Fig. 2. Carbon-13 MAS-NMR spectra of the downfield region of a 68% PVE/32% PIP blend as a function of temperature (K). The two inner peaks correspond to the two unsaturated carbons of PIP and the two outer peaks correspond to the two unsaturated carbons of PVE. Note that the onset of broadening of the carbon resonances associated with PVE occurs at a significantly higher temperature than for those of PIP. This is a consequence of the dynamical heterogeneity of the components in this blend.

Fig. 2), the former interferes with the averaging out of CSA, giving rise to line broadening due to the distribution of chemical shifts. In addition, the  $^1\text{H}$ – $^{13}\text{C}$  nuclear dipolar interactions, manifested in part by the intensities of cross-polarization spectra, cannot be effectively decoupled by radio frequency (RF) irradiation of the protons if molecular motions are occurring at the RF field strength (e.g., 50 kHz). Thus, at temperatures for which motions interfere with the modulation of CSA and dipolar carbon–proton coupling, significant spectral broadening is observed; at higher (lower) temperatures the motions are too fast (slow) to interfere with MAS or RF decoupling. This  $^{13}\text{C}$  NMR technique therefore provides information on local motions and changes thereof associated with blending, and has been applied to a number of polymeric materials previously [19–25].

PVE and PIP exhibit transitions (i.e., NMR line broadening) at 302 and 250 K, respectively, when neat. In Fig. 2 it can be seen that relative to their pure state, the transition temperatures for the blend are shifted closer together. However, they do not occur at the same temperature; the temperature of maximum linewidth is 288 and 266 K for PVE and PIP, respectively. This is direct evidence of heterogeneity of the local dynamics in miscible polymer blends.

Solid state  $^{13}\text{C}$  NMR was recently employed to observe similar differences in the component local dynamics in blends of polyvinylmethylether (PVME) with polystyrene (PS) [24,25]. It is noteworthy that the NMR observations of different local motions have been made on blends, PVE/PIP and PVME/PS, whose viscoelastic spectra exhibit extreme degrees of broadening of the segmental dispersion, along with the reversal of asymmetry in the dispersion curve for viscoelastic relaxation.

### 3. Blend models

A few models have been proposed to quantitatively account for the relaxation behavior in polymer blends and solutions. A most important test of these models is their application to blends, such as PIP/PVE and PVME/PS, in which broad relaxation behavior and asymmetry reversal are found.

#### 3.1. Zetsche and Fischer model

This model [26] focusses on the effect of local composition on the glass transition temperature, and hence on the relaxation dynamics of segments comprising that local environment. The respective components are not assumed to have intrinsically different mobilities. However, since the higher  $T_g$  component will on the average be associated with high  $T_g$  domains (and vice versa for the lower  $T_g$  component), the *mean* relaxation of the components can differ, consistent with the dynamic heterogeneity observed via the  $^{13}\text{C}$  NMR experiments described above [19,24,25]. The broadening towards lower frequency at lower temperatures, as seen in the dielectric loss spectra of PVME/PS blends [1,7] can be reproduced using this approach. The reversal of the characteristic asymmetry of the relaxation dispersion is caused by the divergence in the relaxation times of the components as temperature is reduced.

Application to PIP/PVE blends has likewise shown [13] that the model reproduces the low-temperature broadening. However, the model's results were found to be quantitatively at odds with the relaxation time distributions determined independently by deuterium NMR [13]. This failing was ascribed to the absence of intrinsic mobility differences in the model.

#### 3.2. Lattice model

Jones et al. [27] have developed a model based on a Flory–Huggins-type lattice. Nearest-neighbor contacts are enumerated and their influence on local dynamics assessed. The model has been applied to poly(2,6-dimethylphenylene oxide)/PS blends [28], as well as to polymer/diluent mixtures [29–31]. The analysis yields information concerning local populations and their mobilities. The utility of such information depends on the validity of a lattice approach to chain dynamics, as well as the sensitivity of the calculated results to the assumed population distributions.

#### 3.3. Coupling model as applied to mixtures

This approach is based on the coupling scheme [32,33], in which the shape of the relaxation

function and the temperature dependence of the relaxation time are governed by intermolecular cooperativity. The correlation function for a neat amorphous polymer has the stretched exponential form [34,35], with the observed relaxation time,  $\tau^*$ , depending non-linearly on the strength of intermolecular cooperativity,

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

the latter reflected in the value of the coupling parameter  $n$ . The relaxation time in the absence of intermolecular coupling is  $\tau_0$ , while  $\tau_c$  defines a characteristic time for the onset of the coupling. Note that  $\tau^*$  is usually the experimental observable. However, recent molecular simulations [36] and quasi-elastic neutron scattering results [37] have confirmed the existence of such a temperature independent cross-over time, beyond which intermolecular cooperativity dominates the segmental dynamics.

Since the coupling parameter depends on chemical structure [38-40], the components of a blend have different intermolecular coupling *even when in the same local environment*. This confers a divergence in their relaxation time, as seen from Eq. (1). A priori, a blend model based on the coupling scheme assumes the possibility of different intrinsic mobilities for the components.

Note that the non-linear relationship between coupling strength and relaxation time (Eq. (1)) means that polymer blends are thermorheologically complex. Moreover, since in PVE/PIP blends the more intermolecularly cooperative regions (i.e., those enriched in PVE with higher  $T_g$  and larger  $n$ ) contribute more at low frequency, broadening of the dispersion towards lower frequencies is expected. The asymmetry reversal, as seen in both PVE/PIP and PVME/PS blends, is a natural consequence of the second relation of the coupling model (Eq. (1)).

In addition to this, the components of any mixture experience a distribution of local environments due to composition fluctuations. Chain segments of a given component will experience differing local environments, whereby their relaxation will not be equivalently perturbed by neighboring segments. This means that in mixtures each component will not be associated with a single  $n$  and  $\tau^*$ . For both

components, these will be distributed about values appropriate for the average composition. Of course,  $n$  and  $\tau^*$  are mutually interdependent (Eq. (1)).

The difficulty with a description of blend dynamics based on the coupling model is twofold: (i) the determination of the manner in which local environment alters intermolecular cooperativity and (ii) the manner in which the contributions of various local environments sum to yield the observed macroscopic behavior. To calculate the bulk mechanical response, two extremes can be envisaged, homogeneous stress and homogeneous strain among all local domains. Obviously reality lies intermediate; the mechanical interaction between local environments is more complicated. For the dielectric response, the simple, linear summation of the local responses may be appropriate, and in fact analysis of dielectric data employing this assumption have been carried out for PVME/PS [7], TMPC/PS [6] and PIP/PVE blends [41].

To demonstrate the blend model based on the coupling scheme, an analysis of dynamic mechanical data on PIP/PVE blends has been carried out [2]. The calculations were done by assuming concentration fluctuations produce a normally distributed range of values for the coupling parameters of each component. In the limit of homogeneous strain, the relaxation modulus for the  $i$ th component is taken to be

$$E_i(t) = E_i(0) \int_0^1 \exp(-a_i(n - n_i)^2) \times \exp\left(-\frac{t}{\tau_i^*(n)}\right)^{1-n} dn, \quad (2)$$

where  $\tau^*$  is calculated for each  $n$  (the latter varying for each component with local composition) using Eq. (1). In Eq. (2),  $n_i$  represents the mean value of the coupling parameter for component  $i$  and  $a_i$  is a measure of the concentration fluctuations. The effective relaxation times of the segments are determined from Eq. (2) using  $\omega_c = 10^{10} \text{s}^{-1}$ . The transform of Eq. (2), in conjunction with Eq. (1), allow a calculation of  $E''(\omega)$  for the mixtures.

As referred to above, a composition with 75% PVE has a segmental relaxation peak too broad to be completely measured at a single temperature.

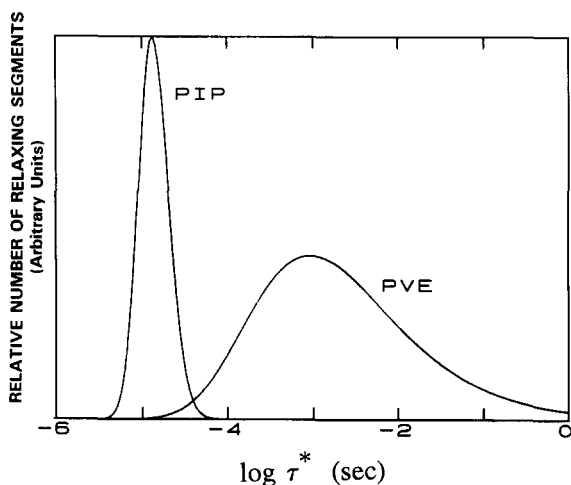


Fig. 3. The relaxation time distribution determined (using Eqs. (2) and (3)) from dynamic mechanical measurements on a blend of PIP with 75% PVE. The components differ in both their mean relaxation time, as well as the distribution. The latter is broader for the PVE component due to its stronger intermolecular coupling.

Notwithstanding the thermorheological complexity of miscible blends, time-temperature superpositioning was employed [2] to yield an approximation to the peak shape. The obtained value of the components' relaxation times, necessary to fit the mechanical spectra (such as seen in Fig. 1), are shown in Fig. 3. Due to its stronger coupling, the PVE has longer relaxation times and a broader distribution. The latter feature is a direct consequence of the non-linear dependence of  $\tau^*$  on  $n$  (Eq. (1)). It should also be stressed that the distribution of  $\tau^*$  seen in Fig. 3 is due to the distribution of local environments. This inhomogeneous line broadening is a feature specific to blends. In a neat material, relaxation of macroscopic variables such as stress is homogeneous as a result of averaging of the different relaxation times associated with individual molecules or segments.

#### 4. Conclusions

The results of solid state NMR experiments and dynamic mechanic spectroscopy make clear that miscible polymer blends can display new physics,

not to be found in neat materials. The morphological heterogeneity occasioned by concentration fluctuations, along with the dynamic heterogeneity caused by intrinsic differences in component mobilities, give rise to segmental relaxation functions having unusual shapes and temperature dependences. Application of a model for blends based on the coupling scheme can successfully describe the prominent features of experimental results.

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