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Component Dynamics in Polyisoprene/Poly(vinylethylene) Blends

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Introduction

For many years the blending of polymers has been pursued to obtain useful new materials. More recently it has been recognized that the often unusual behavior of blends can provide new insights into polymer physics. Among the many miscible polymer blends, one of the most interesting is the mixture of polyisoprene (PIP) with poly(vinylethylene) (PVE). Miscibility occurs over the entire composition range despite an absence of specific (chemical) interactions between the components.[1,2] Certainly, it is advantageous to investigate systems in which the structure and dynamics are not complicated by specific interactions.

The study of blends is particularly fruitful when the constituent dynamics can be resolved; for example, the relaxation behavior of one component can be examined as a function of its concentration in the blend. Solid-state ^{13}C NMR can be used to monitor the dynamics of the individual components by exploiting differences in their chemical shifts. The first application of temperature-dependent solid-state ^{13}C NMR to polymer blends was, in fact, a study of PVE/PIP mixtures.[3] It was found that, despite the blend's single macroscopic glass transition temperature, local segmental motions of the PIP and PVE have different mean relaxation times and temperature dependencies. The broad glass transitions observed for this blend in DSC and thermal expansivity measurements[4,5] were shown to be correlated with the temperature dependence of the ^{13}C NMR spectra.[3] Subsequently, a model for the segmental dynamics in miscible blends was proposed,[6] wherein the intrinsic differences in the components' mobility, together with the effect of local environment, were shown to govern the shape, composition dependence, and temperature dependence of the segmental relaxation function. Initially applied to the PIP/PVE system,[6] the model has been extended to other miscible blends.[7–9] The basic concepts underlying this model have been directly corroborated by recent ^{2}H NMR experiments on the same blend of PIP and PVE.[10]

More detailed information concerning the segmental dynamics in the PVE/PIP blend has been obtained from the combined use of dielectric and mechanical spectroscopies.[11] Taking advantage of differences in the relative contribution of PIP and PVE to mechanical and dielectric responses, the respective segmental relaxation times of each component were measured as a function of temperature for various compositions. This data[11] revealed the disparate manner in which changes in local concentration affect the motions of the respective components.

Very recently, similar information on the same blend has been extracted from two-dimensional ^{2}H NMR measurements.[12] Again the mean relaxation time for each component was determined as a function of temperature for various blend concentrations. The purpose of this paper is to compare the results from these two very different approaches to resolving component dynamics. Analysis of this existing data is intended to determine the extent of their agreement, which is an important issue in assessing any interpretation of the interesting behavior seen in miscible blends of PIP and PVE.

Results and Discussion

By taking advantage of the prominence of the PIP component's contribution to dynamic mechanical relaxation and the PVE component's contribution to dielectric relaxation, the respective segmental relaxation dynamics in the blend were resolved, at least for compositions having 20% or more of the PVE.[11] Five blends, designated PVE-75, PVE-50, PVE-25, PVE-20, and PVE-15, where the number denotes the percentage of weight of the PVE, together with neat PIP and PVE were studied. The obtained values for the segmental relaxation times of PIP and PVE at various temperatures and compositions are reproduced in Figures 1 (PVE) and 2 (PIP). The results are displayed in the form of fragility (or cooperativity) plots, that is, T_g-scaled Arrhenius plots of the segmental relaxation times. This method of presenting the data has been demonstrated to be a self-consistent means to compare and distinguish the segmental relaxation behavior of different polymers.[13–15] In particular, it illustrates the correlation existing for amorphous polymers and glass-forming small-molecule liquids between the shape of the relaxation function and the magnitude of time–temperature shift factors. Broader relaxation functions (e.g., broader dispersions in the dielectric loss or the mechanical loss modulus) are associated with a mean relaxation time that changes more with T_g-scaled temperature (or reciprocal temperature). This correlation, an extant prediction of the coupling model of relaxation,[16] reflects the effect of intermolecular cooperativity on the local dynamics.

From the results of the combined mechanical and dielectric spectroscopic data, the following conclusions were drawn:[11]

(1) The concentration fluctuations inherent to miscible blends cause the degree of intermolecular cooperativity of the motions of each component to differ from one another as well as to differ from that associated with the neat state.

(2) Each component has its own most probable relaxation time, reflecting that component in its most probable local composition. The corresponding relaxation function of each component has its own distribution, determined both by the nature of the intermolecular cooperativity it experiences and by the manner in which local composition alters this cooperativity. Given the correlation between relaxation time and temperature dependencies, it follows that each component will have a different temperature dependency for its most probable relaxation time.

(3) Each component's relaxation function, inhomogeneously broadened due to the distribution in local environments, is thermorheologically complex. This is a direct consequence of the distribution in local intermolecular cooperativity, and hence in temperature dependencies, effected by the various local environments. This means, of course, that the measured relaxation function, reflecting the contribution of both components, will not exhibit time–temperature equivalence. Specifically, an asymmetric broadening toward lower frequency arises as temperature is lowered (see also refs 6–9).

Chung et al.[12] were also able to determine, using two-dimensional deuteron exchange NMR (^{2}H NMR) data,

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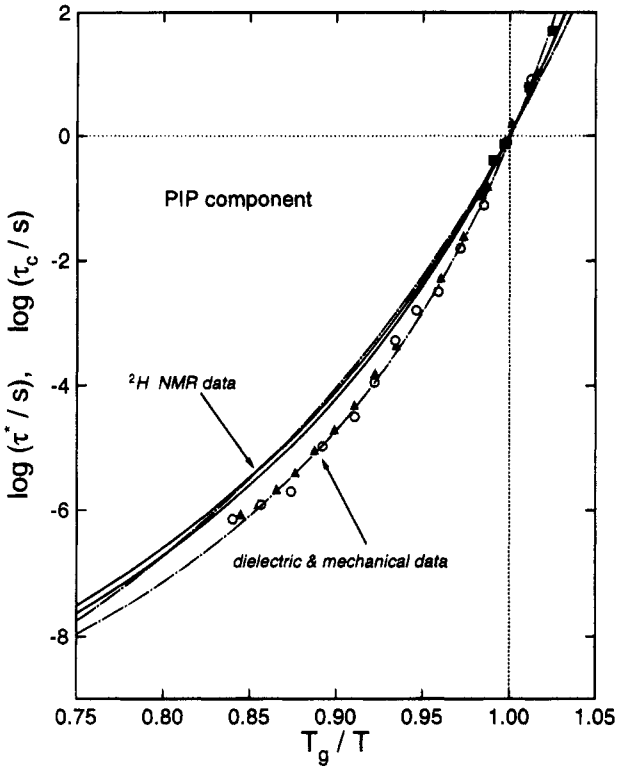

Figure 1. Mean segmental relaxation times for PIP in blends containing 0, 25, and 50% by weight of PVE, determined using deuterium NMR and by combined dielectric and mechanical spectroscopies. The data, displayed in the form of cooperativity plots, demonstrate the insensitivity of the PIP component dynamics to local composition.

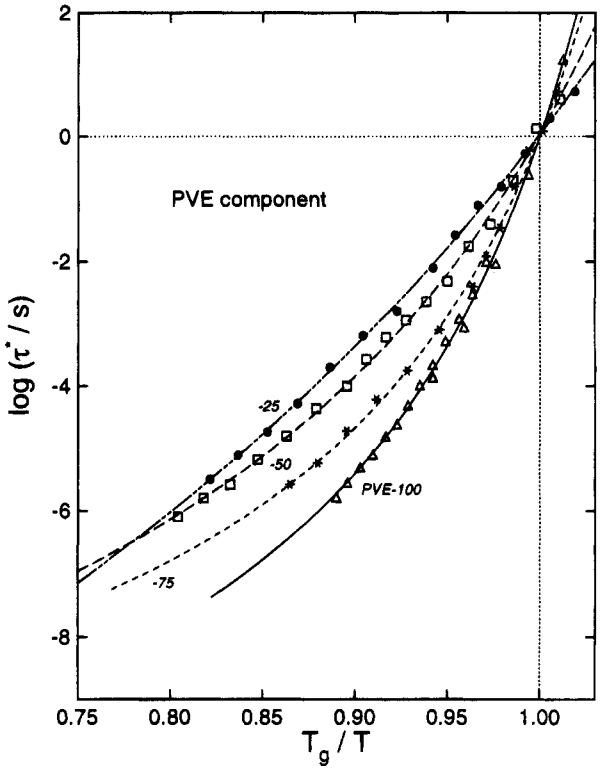

Figure 2. Cooperativity plots of the mean segmental relaxation time of PVE in blends with PIP having the indicated concentration of PVE. As the PVE is diluted with PIP, there is a systematic decrease in its T_g-normalized temperature dependence, reflecting a reduction in intermolecular constraints on the PVE local motion. This is in contrast to the behavior of PIP shown in Figure 1.

the average relaxation time of each component in PIP/PVE mixtures having PVE weight fractions of 25, 50, and 75%. Thus, the compositions of the blends measured by ^{2}H NMR are identical to those investigated using dielectric and mechanical spectroscopies.[11] The neat PVE and PIP used in both studies were of high molecular weight, thus having almost the same calorimetric glass transition temperatures. These conditions make possible a direct comparison between the results of the two experimental investigations. The mean correlation time, τ_c, reported from the ^{2}H NMR[12] and the most probable relaxation time, τ^*, from dielectric relaxation (DR) and mechanical relaxation (MR) measurements[11] are close in value, but they are not identical. The small differences are probably due to slight differences in the microstructure (1,2-, *cis*-1,4-, or *trans*-1,4-addition product) of the samples used in the two studies. In addition, there is no reason to expect that τ_c and τ^* would be the same, even on the same sample, because ^{2}H NMR and DR or MR may not probe the same correlation function of the local segmental motion. From the temperature dependence of τ_c for each component in the blend, fitted by the Vogel–Fulcher[11] or equivalent WLF[12] equation, we can find for each composition the temperatures, $T_{g,PIP}$ and $T_{g,PVE}$, at which τ_c assumes the value of an arbitrarily long time, e.g., 1 s. Similarly, we can determine these "glass temperatures" from the DR and MR times, τ^*, for each of the same compositions. The "glass temperatures" so obtained (Tables 1 and 2) are close to each other but not identical.

In view of the subtle differences between the two sets of data, the best we can do to compare τ_c and τ^* is to plot them against the normalized reciprocal temperature, $T_{g,PIP}/T$ and $T_{g,PVE}/T$ for PIP and PVE, respectively. This is shown for the segmental relaxation of the PIP component in several blends in Figure 1. The important feature is that the T_g-scaled temperature dependences of τ_c and τ^* for the PIP component are quite similar, and both are insensitive to the concentration of PVE up to 50% of PVE. Similarly, we have plotted the T_g-scaled temperature dependences of τ_c and τ^* for the PVE component in the blends, separately in Figures 2 and 3. In contrast to the behavior of the PIP component, the T_g-scaled temperature dependence of the PVE component changes significantly with the weight fraction of PVE. Both ^{2}H NMR and DR data exhibit this effect and quantitatively almost in identical fashion. Thus, there is remarkable agreement in the results obtained by two very different approaches—^{2}H NMR spectroscopy[12] and a method relying on combined dielectric and mechanical measurements.[11]

Table 1. Glass Transition Temperature (K) of PVE Component

blend	^{2}H NMR T_g	dielectric/mechanical T_g
PVE-100	273.6	271.4
PVE-75	253.5	253.4
PVE-50	236.8	235.9
PVE-25	227.2	224.6

Table 2. Glass Transition Temperature (K) of PIP Component

blend	^{2}H NMR T_g	dielectric/mechanical T_g
PVE-75	236.7	not determinable
PVE-50	226.2	219.4
PVE-25	218.5	216.8
PVE-0	212.3	210.5

This agreement means that the explanation of the dielectric and mechanical data offered in ref 11 applies

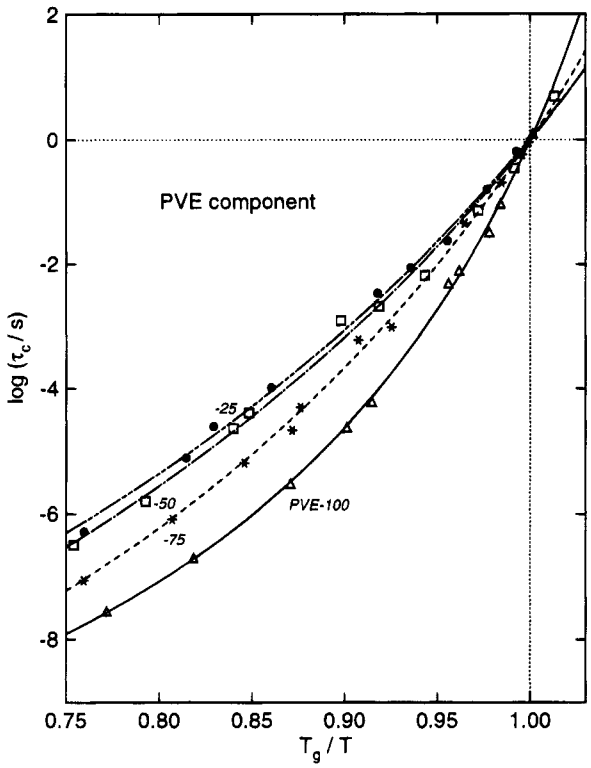

Figure 3. Cooperativity plots of the correlation time determined by deuterium NMR spectroscopy for PVE in blends with PIP of the indicated concentrations of PVE. In near-quantitative agreement with the results in Figure 2, the PVE exhibits a range of segmental relaxation behavior as the blend composition is varied.

verbatim to the ^{2}H NMR data of Chung et al. In Figures 2 and 3, it can be seen that as PVE is diluted with PIP, the cooperativity of its segmental relaxation is reduced; that is, the relaxation time has a weaker dependence on temperature, implying that the segmental relaxation function for the PVE in the blend becomes narrower. Of course, the observed dispersion in G'' or ϵ'' is the heterogeneous superposition of the contribution from both components, each experiencing a distribution in local environment and hence in degree of intermolecular cooperativity. Hence, changes in the inherent relaxation behavior of one component are not necessarily reflected in corresponding changes in the measured relaxation function.

In any of these blends the fragility of PVE is less than that of neat PVE (Figure 2). This is expected, since in any local composition the replacement of PVE by the more mobile PIP mitigates the dynamic intermolecular constraints. Contrarily, PIP, whose local segmental relaxation is only weakly intermolecularly coupled even when neat, experiences only a modest alteration in fragility when blended with PVE (see Figure 1). The greater mobility of the PIP is due to its smaller local friction factor (lower T_g and smaller noncooperative relaxation time) and weaker capacity for intermolecular coupling.[17] Hence, it is not surprising that the curves (Figure 1) for PIP in the different blend concentrations span only a very small range of cooperativities.

The bulk relaxation of the blend reflects the combination of the components' contributions. Their distinctly different relaxation behavior gives rise to the striking features of the blend in the glass transition zone—the anomalously broad glass transition[4,5] and the peculiar skewing of the T_g dispersion toward lower frequency.[6,9] The asymmetry reflects the distribution in the intermolecular cooperativity for local segmental relaxation resulting from composition fluctuations in the blend. Its amplification as temperature is lowered is a direct consequence of the stronger cooperativity of PVE in comparison to PIP (i.e., the greater dependence of τ on T_g/T) seen in Figures 1–3.

Note added in proof: It was recently suggested (Katana, G.; Fischer, E. W.; Hack, Th.; Abetz, V.; Kremer, F. *Macromolecules* **1995**, *28*, 2714) that application of our model of blend dynamics might be restricted to thermorheologically simple systems. In fact, an extant prediction of our blend model is the breakdown of the time–temperature superposition principle for segmental relaxation in miscible blends.[6] While not always experimentally observable, most miscible blends are in fact thermorheologically complex.

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