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Dynamics of a poly(isoprene)/poly(vinyl ethylene) blend revisited: Component polymer relaxation and blend behavior

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Abstract

Motivated by recent molecular dynamics simulation studies of miscible blends of dynamically disparate polymers, we have revisited the experimentally measured dielectric relaxation in a 50/50 blend of poly(isoprene) and poly(vinyl ethylene) (PI/PVE). In contrast to efforts to explain the dielectric loss in PI/PVE blends in terms of a distribution of local environments leading to a broad distribution of segmental relaxation times (the so-called concentration fluctuation model), our analysis indicates that there is no evidence for significant broadening of the relaxation processes in the component polymers upon blending. Rather, we find that the dielectric loss of the 50/50 PI/PVE blend can be represented as a sum of α- and β-relaxation processes for the component polymers represented with Havriliak–Negami functions whose shape and relaxation strength are consistent with those obtained for the pure PI and PVE melts. The α-relaxation process for the PVE component was found to be dramatically influenced by blending, moving to much higher frequency with moderate narrowing, while the α-relaxation process for the PI component shifted to somewhat lower frequency with slight broadening, consistent with our MD simulations of a model blend and 2D NMR measurements on PI/PVE blends. In contrast, the β-processes in the PVE and PI components were found to be essentially uninfluenced by blending, with the latter accounting for the significant high-frequency loss observed in the PI/PVE blend.

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Keywords: Polymer blends; Dielectric relaxation; α-relaxation process; β-relaxation process

1. Introduction

The ability to understand and predict the behavior of miscible polymer blends based upon the behavior of the pure component polymers comprising the blend is central to designing blends with desired properties. Understanding the dynamics of miscible polymer blends may also have significant impact on our understanding of other dynamically heterogeneous polymer systems such as polymer nanocomposites, microphase separated polymer blends and polymers in confined environments.

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Extensive studies utilizing dielectric spectroscopy, NMR, dynamic neutron scattering, and DSC techniques have been conducted on a wide variety of miscible polymer blends [1–6] providing important insight into the influence of blending on segmental and terminal relaxation of their components. However, despite this substantial body of experimental work, our understanding of how blending influences segmental relaxation processes is far from complete.

Furthermore, none of the several phenomenological models that have been proposed to describe, explain and predict segmental dynamics of polymer components in miscible blends appears to fully capture the physics of these complex materials. The Lodge–McLeish model [7] and various types of concentration fluctuation (CF) models [8–10] have been extensively applied to description of component dynamics in polymer blends. However, while these models, which are based on relatively simple concepts and well-defined physical phenomena, have been able to fit experimental data for a number of blends, this often requires using parameters that are physically unreasonable. The coupling model (CM) [11], which provides a relationship between the primary and secondary relaxation processes in polymer and glass-forming liquids and melts, has not found wide application in the description of the dynamics in polymer blends despite the claim that the model can explain all experimentally observed phenomena in miscible polymer blends as well as other glass-forming liquids. Recently, we have shown that CM predictions of correlations between the α-relaxation and β-relaxation processes in blends are inconsistent with molecular dynamics simulations of simple model blends [12].

Validation, comparison and further improvement of theoretical models are further complicated by an apparent inconsistency of reported data for some polymer blends obtained by different experimental techniques for the same system. One of the primary examples of such controversy is still unresolved for the segmental dynamics in one of the most studied miscible blends, poly(isoprene)/poly(vinyl ethylene) (PI/PVE). Several 2D NMR measurements [13] for this blend at temperatures below 240 K have shown that upon blending the segmental dynamics in the low T_g (glass transition temperature) component (PI) slow down significantly (about two orders of magnitude) relatively to the pure PI melt while the segmental dynamics of the high T_g component (PVE) speeds up by several orders of magnitude relatively to its pure melt. Segmental dynamics of the PI and PVE components in the blend showed different temperature dependences each having its own glass transition temperature. However, while dielectric spectroscopy measurements [14–16] have shown some consistency with predictions of 2D NMR, e.g., similar temperature dependence of segmental dynamics of the components [17], they have also found features that appear to be inconsistent with the 2D NMR results. In Fig. 1, dielectric loss data [16] for a 50/50 PI/PVE blend at 270 K are shown together with the dielectric loss of pure PI and PVE melts at the same temperature. The dielectric response of the blend is very broad and has a double-peak structure with the low frequency peak positioned roughly in between the peaks for pure components while the second peak overlaps with the frequency range covered by the response of the pure PI melt. This high-frequency part of the blend response has been associated with the segmental relaxation of the PI component and it was concluded that PI segmental relaxation does not change (relatively to the relaxation in the pure PI melt) upon blending with PVE at 270 K [16]. However, extrapolation of 2D NMR results to this temperature indicates that segment dynamics of PI component in the 50/50 PI/PVE blend should slow down by at least a factor of six relatively to its pure melt.

A recent attempt [18] to describe the dielectric relaxation data for PI/PVE blends at 270 K using a CF model did not provide a satisfactory description. In that work, a simple lattice model was used to predict a distribution of local environments for

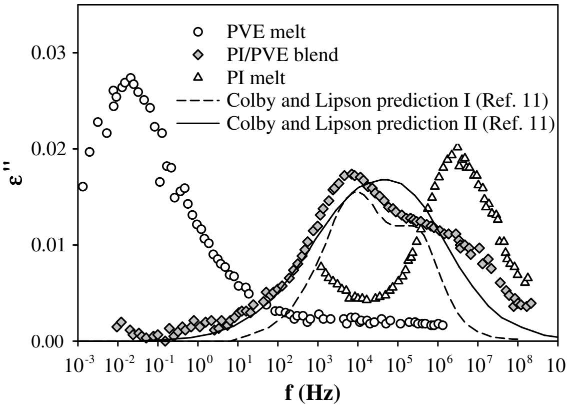

Fig. 1. Frequency dependence of dielectric loss for PI melt (triangles), PVE melt (circles), and a PI/PVE 50/50 blend (diamonds) at 270 K. All data are from Arbe et al. [16]. Two predictions for the blend response using the CF model from Colby and Lipson [18] are also shown with lines.

the CF model which then coupled with the dynamic scaling approach was used to generate the dielectric spectrum for the PI/PVE blend. The two best predictions of dielectric loss for a 50/50 PI/PVE obtained in that study are also shown in Fig. 1. Unlike many CF models, where non-physical distributions of local environments have to be assumed to provide an adequate description of experimental data (see discussion below), the parameters and distribution functions used in this work were physically reasonable. However, the model clearly fails to capture the high-frequency response of the blend.

The absence of clear understanding for the source and the underlying mechanism(s) responsible for the high-frequency wing in the dielectric response of the PI/PVE blend as well as its apparent inconsistency with 2D NMR have motivated us to reconsider the analysis of dielectric response in this blend using the insight obtained from our recent molecular dynamics simulations of model polymer melts and blends. In this work, we show how the dielectric response of the 50/50 PI/PVE blend can be reproduced in a way which is consistent with the results obtained for the pure melt components and from 2D NMR blend measurements and without involving any concepts of compositional heterogeneities.

2. Mechanisms of segmental relaxation in model polymer melts and blends

Our recent molecular dynamics simulation studies of pure melts of 1,4-polybutadiene (chemically realistic polybutadiene, or CR-PBD) and a dynamically fast 1,4-polybutadiene (low barrier polybutadiene, or LB-PBD) revealed the presence of two relaxation processes in these polymer melts.[19] Here, LB-PBD is identical to CR-PBD except that the dihedral barriers have been lowered, resulting in significantly faster segmental dynamics. The α-, or primary, relaxation process in these polymer melts was found to follow time–temperature superposition with a Vogel–Fulcher temperature dependence while the β-relaxation process was found to be a local, backbone-engendered secondary process that exhibits Arrhenius temperature dependence and both weakens and broadens with decreasing temperature. One of the most important conclusions made from these MD simulations studies of pure melts is that the α- and β-relaxation processes do not merge at high (above T_g) temperatures. While our simulations clearly showed that with increasing temperature the separation between the characteristic relaxation times of the α- and β-relaxation processes decreases, leading to overlap of the processes, the mechanism responsible for each process is still operative at high temperatures and both processes remain active. Moreover, at high temperatures (above T_g) the strength of the β-relaxation process can become comparable (or even larger) than that for the α-relaxation process. Similar conclusions have been previously discussed in the interpretation of experimental dielectric response data for PBD melts by Arbe et al. [20].

Recently, we have also carried out molecular dynamics simulation studies of a 50/50 blend of CR-PBD ($T_g = 164$ K) and LB-PBD ($T_g = 108$ K) [12,21]. Fig. 2 shows the dielectric loss in CR-PBD and LB-PBD melts as well as in the 50/50 CR-PBD/LB-PBD blend at 198 K along with the contributions from the α- and β-relaxation processes for the dynamically fast LB-PBD. For the dynamically slow (CR-PBD) component of the 50/50 blend the α- and β-relaxation processes, while both active, cannot be uniquely resolved due to limited separation of the processes. Hence, we represent the dielectric

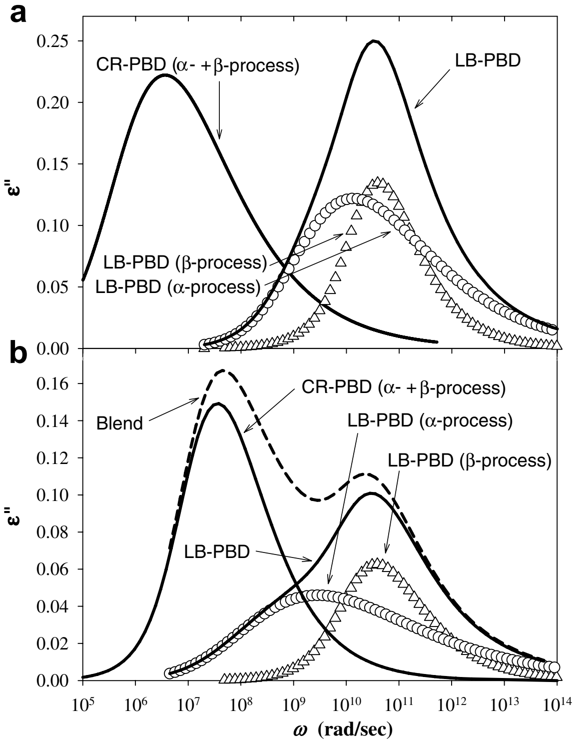

Fig. 2. Dielectric loss in: (a) pure CR-PBD and LB-PBD melts and (b) a CR-PBD/LB-PBD 50/50 blend at 198 K. Also shown are contributions from the α-relaxation and β-relaxation processes for LB-PBD. Data are from Bedrov and Smith [12].

loss of CR-PBD in both the pure melt and the blend as a combined α-relaxation and β-relaxation process. Our simulation studies of this model blend revealed that in order to understand segmental relaxation in the blend one needs to take into account the presence of α- and β-relaxation processes in the pure component polymers, and how these processes are influenced by blending. Compared to the pure CR-PBD and LB-PBD melts, the main characteristics of dielectric relaxation in 50/50 blend can be summarized as follows:

1. The combined α- and β-process for the dynamically slow component (CR-PBD) shifts to significantly higher frequency and narrows moderately.
2. The α-process for the dynamically fast component (LB-PBD) shifts dramatically to lower frequency and shows significant broadening.
3. The β-process for the dynamically fast component (LB-PBD), which is comparable in strength to the α-process at 198 K (well above the T_g of LB-PBD), is essentially uninfluenced by blending, maintaining the shape, principal relaxation time and strength observed in the pure melt.

The similarity in the dielectric response of the 50/50 PI/PVE blend (Fig. 1) and our model 50/50 CR-PBD/LB-PBD blend (Fig. 2) is striking. Given this apparent correspondence, we hypothesize that the mechanisms of segmental relaxations governing the dielectric response in the PI/PVE blend are similar to those observed in MD simulations of the CR-PBD/LB-PBD blends. Specifically, we assume that at temperatures well above the T_g of PI that the β-relaxation process (associated with the polymer backbone motion) in the PI melt is comparable in strength to the α-relaxation process and does not change in strength, shape or principal relaxation time upon blending, and therefore is largely responsible for the high-frequency peak (wing) in the dielectric response of the blend. Exploring this supposition, we have carried out an analysis of dielectric loss in a 50/50 PI/PVE at 270 K blend utilizing data for pure component melts of PVE and PI in order to determine if the blend dielectric response can be understood in terms of the response of the pure components to blending consistent with the observation enumerated above for our model CR-PBD/LB-PBD blend and in a manner consistent with 2D NMR measurements.

3. Analysis of dielectric loss in a PI/PVE blend and its components

3.1. PI melt

Recently dielectric measurements on PI melts at low temperature and high frequency have revealed the presence of a β-relaxation process [22] that has been clearly associated with the backbone segmental motion and not with rotation of pendant methyl group. We have analyzed the dielectric loss in PI melts in the temperature range of 204–216 K obtained from these measurements in terms of a sum of two Havriliak–Negami (HN functions) [23]

$$\varepsilon^*(f) = \Delta\varepsilon_\alpha \frac{1}{[1+(2\pi i f \tau_a)^{\alpha_\alpha}]^{\gamma_\alpha}} + \Delta\varepsilon_\beta \frac{1}{\left[1+\left(2\pi i f \tau_\beta\right)^{\alpha_\beta}\right]^{\gamma_\beta}} \quad (1)$$

Here, $\varepsilon^*(f)$ is the frequency dependent complex dielectric constant, $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\beta$ are the relaxation strengths of the α- and β-relaxation processes, τ_α and τ_β are the principal relaxation times for the two processes, while α_α, γ_α and α_β, γ_β are the HN width and asymmetry parameters for the two processes. The frequency dependent dielectric loss is given by the imaginary part of the complex dielectric constant. We found that a good representation of the frequency dependent dielectric loss in the PI melt could be obtained by utilizing temperature-independent shape parameters for the α-relaxation process ($\alpha_\alpha = 0.85$, $\gamma_\alpha = 0.48$), implying that time-temperature superposition holds for the α-relaxation process in PI melts. For the β-process we constrained $\alpha_\beta = \gamma_\beta$. The resulting representation of experimental dielectric loss in PI melts is shown in Fig. 3. The principal relaxation times (τ_α and τ_β) are shown in Fig. 4a while the shape parameters and the relative strength of the β-relaxation process are shown Fig. 4b.

Based upon our successful representation of the dielectric loss in PI melts at low temperatures with a sum of two HN functions, we proceeded to represent the dielectric loss in the PI melt at 270 K as a sum of α- and β-relaxation processes (Eq. (1)). A similar approach was taken in analysis of the experimentally measured dielectric loss in pure 1,4-polybutadiene (PBD) [20] where it was found that at temperatures above the glass transition temperature two processes, while not leading to two separated loss peaks, remain operative and that the β-relaxation process is comparable or even greater in strength than the α-relaxation process. As discussed above, our analysis of dielectric relaxation of LB-PBD melts from MD simulations also revealed separate α- and β-relaxation processes dominated at higher temperatures by the β-relaxation. Consistent with analysis of dielectric loss in PBD [20] we assumed that the shape parameters for the α-relaxation process in PI remain independent of temperature, i.e., we used $\alpha_\alpha = 0.85$ and $\gamma_\alpha = 0.48$ as obtained from analysis of the low temperature PI melt data discussed above. We also assumed $\alpha_\beta = \gamma_\beta$ for the β-relaxation process in PI at 270 K as was done for lower temperatures. The strengths of the α- and β-relaxation processes, ($\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\beta$), were treated as adjustable parameters and were fit simultaneously with the strengths of the PI α- and β-relaxation processes in the 50/50 blend (see below). Consistent with our simulations of LB-PBD melts [19] as well as dielectric relaxation studies of PBD melts [20], we find that the strength of the β-relaxation process in the PI melt is comparable to that of the α-relaxation process at 270 K, well above T_g of PI. The resulting representation of the dielectric loss in the PI melt at 270 K is shown in Fig. 5 along with the individual contributions of the α- and β-relaxation processes. The resulting HN parameters are given in Table 1. Fig. 4 reveals that the shape of the β-relaxation process, its strength, and the principal relaxation times obtained at 270 K for the PI melt are consistent with those obtained for the lower temperature PI melts.

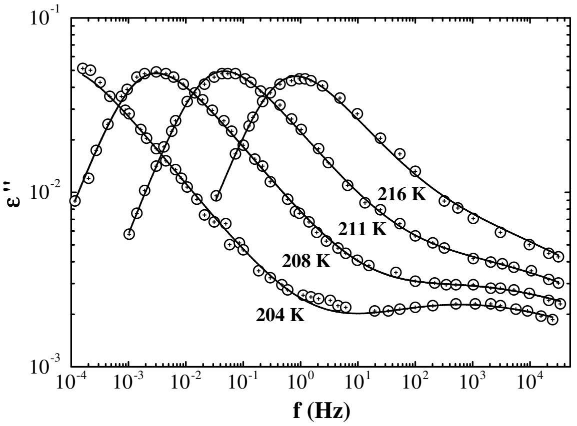

Fig. 3. Dielectric loss in a PI melt over a temperature range of 204–216 K, from Roland et al. [22]. Solid lines are a fit of Eq. (1) to the experimental dielectric loss.

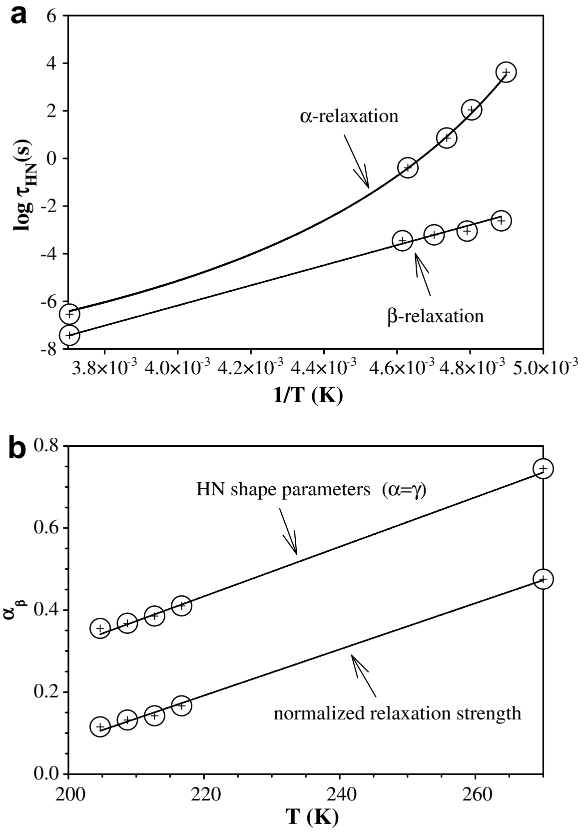

Fig. 4. (a) Principal relaxation times for the α- and β-relaxation processes in PI melts obtained by fitting Eq. (1) to experimental relaxation data. The solid lines are Vogel–Fulcher (α-process) and Arrhenius (β-process) fits utilizing all data shown. (b) The HN shape parameter ($\alpha = \gamma$) and relative strength [$\Delta\varepsilon_\beta/(\Delta\varepsilon_\beta + \Delta\varepsilon_\alpha)$] for the dielectric β-relaxation process in PI melts. The solid lines are linear fits in temperature utilizing all data shown.

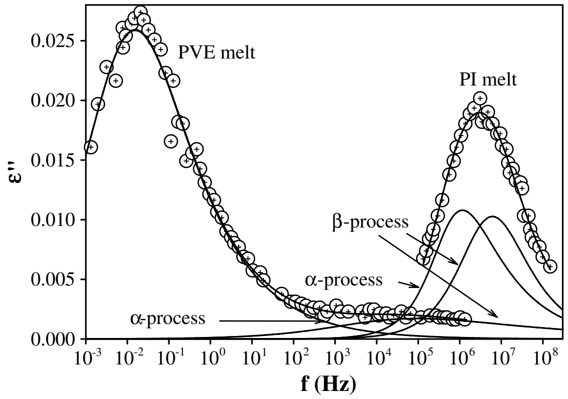

Fig. 5. Experimental frequency dependent dielectric loss for PVE and PI melts at 270 K from Arbe et al. [16]. Only experimental data points used in fitting of α- and β-relaxation processes (Eq. (1)) are shown. The lines show the contributions of the α- and β-relaxation processes to the dielectric relaxation of the pure components.

Table 1
HN fitting parameters at 270 K for a 50/50 PI/PVE blend and pure component melts

System	Process							
	β				α			
	τ_{HN} (s)	α	γ	Δε	τ_{HN} (s)	α	γ	Δε
Pure melts								
PVE	1.97 E−5	0.381	0.381	0.0166	2.36 E+1	0.552	0.615	0.135
PI	3.69 E−8	0.745	0.745	0.0349	2.86 E−7	0.85	0.48	0.0385
50/50 blend								
PVE	1.97 E−5	0.381	0.381	0.0083	5.24 E−5	0.622	0.695	0.0677
PI	4.19 E−8	0.745	0.745	0.0175	1.71 E−6	0.851	0.334	0.0193

3.2. PVE melt

Fig. 5 reveals that the α- and β-relaxation processes in PVE at 270 K are well-separated and that the dielectric loss can be well represented as a sum of two HN functions (Eq. (1)) whose parameters are given in Table 1. As with PI, we constrained $\alpha_\beta = \gamma_\beta$ for the β-relaxation process in the PVE melt. Consistent with previous analysis of dielectric loss in PVE [16] we find the β-process to be very broad with a strength about 10% of that for the α-process (see Table 1).

3.3. 50/50 PVE/PI blend

We represent the complex dielectric constant in the 50/50 PI/PVE blend as

$$\varepsilon^*(f) = \left[\Delta\varepsilon_\alpha \frac{1}{[1+(2\pi i f\tau_a)^{\alpha_\alpha}]^{\gamma_\alpha}} + \Delta\varepsilon_\beta \frac{1}{[1+(2\pi i f\tau_\beta)^{\alpha_\beta}]^{\gamma_\beta}}\right]_{\text{PVE}} + \left[\Delta\varepsilon_\alpha \frac{1}{[1+(2\pi i f\tau_a)^{\alpha_\alpha}]^{\gamma_\alpha}} + \Delta\varepsilon_\beta \frac{1}{[1+(2\pi i f\tau_\beta)^{\alpha_\beta}]^{\gamma_\beta}}\right]_{\text{PI}} \quad (2)$$

where the subscript (PVE or PI) indicates the contribution of the PVE and PI components, respectively, which are each represented as the sum of two HN functions. In Fig. 6 we show the representation of the dielectric loss in the 50/50 PI/PVE blend obtained with the HN parameters given in Table 1. Here we assumed that

(1) The β-relaxation process in both components is essentially uninfluenced by blending. For PVE, we utilized the same strength,[1] shape and principal relaxation time as obtained for the PVE melt at 270 K. For PI, the strength of the β-relaxation process was determined simultaneously in the blend and the melt (along that of the α-process) and was assumed to be uninfluenced by blending as was the shape of the β-relaxation. The principal relaxation time for the β-relaxation process in PI was an adjustable parameter in the fitting of the dielectric loss in the blend.

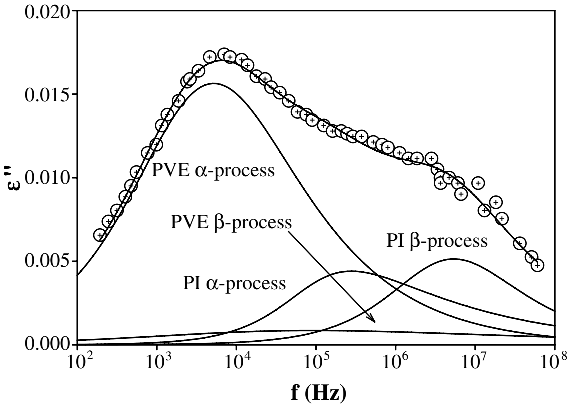

Fig. 6. Representation of experimental dielectric loss in a 50/50 PI/PVE blend from Arbe et al. [16] at 270 K using Eq. (2) with constrains as described in the text. The lines show the total dielectric loss and the contributions for the α- and β-relaxation processes for the two blend components.

(2) The shape of α-relaxation process in both components was allowed to change on blending as were the principal relaxation times. Extrapolation of segmental relaxation times obtained from 2D NMR measurements at lower temperature [13] to 270 K as well as diffusion measurements [25] at 270 K on 50/50 PI/PVE blends and PI melts indicate that the local dynamics of PI slow down by a factor of about six upon blending. We therefore introduced $\tau_\alpha\,(\text{PI})_{\text{blend}} = 6\tau_\alpha\,(\text{PI})_{\text{melt}} = 1.71 \times 10^{-6}$ s as a constraint in our representation of the dielectric loss of the 50/50 PI/PVE blend. Here, $\tau_\alpha\,(\text{PI})_{\text{melt}}$ is

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[1] The relaxation strengths for the four processes in the blend were taken as 50% of those obtained in the pure melt as can be seen in Table 1.

the principal relaxation time obtained from our fitting of the pure melt dielectric loss. No constraint was placed on τ_α (PVE)$_{\mathrm{blend}}$. The relaxation strength for the α-relaxation process for PVE in the blend was taken as that obtained for the pure melt. For PI, the strength of the α-relaxation process was determined simultaneously in the blend and the melt (along that of the β-process) and was assumed to be uninfluenced by blending.

4. Discussion and conclusions

The relaxation times for the α- and β-relaxation processes in the pure melts and the 50/50 PI/PVE blend, resulting in the agreement with experiment for the dielectric loss in the melts shown in Fig. 5 and in the blend shown in Fig. 6, are shown in Fig. 7. Also shown in Fig. 6 are the contributions of α- and β-relaxation processes of the PI and PVE components to the total dielectric loss of the blend. We find that dielectric relaxation in the PVE and PI components of the 50/50 PI/PVE blend is consistent with the behavior of CR-PBD and LB-PBD observed in our simulations of a 50/50 CR-PBD/LB-PBD blend enumerated above as well as in 2D NMR studies of a 50/50 PI/PVE blend [13]. Specifically,

(1) The high-frequency dielectric loss in the PI/PVE blend is due largely to the β-relaxation of the dynamically fast PI component that is strong at temperatures above the glass transition of pure PI and whose shape, strength and principal relaxation time (see Fig. 7) are largely uninfluenced by blending. While we allowed the principal relaxation time for the β-relaxation in the PI component to shift upon blending, Table 1 and Fig. 7 reveal almost no change upon blending.

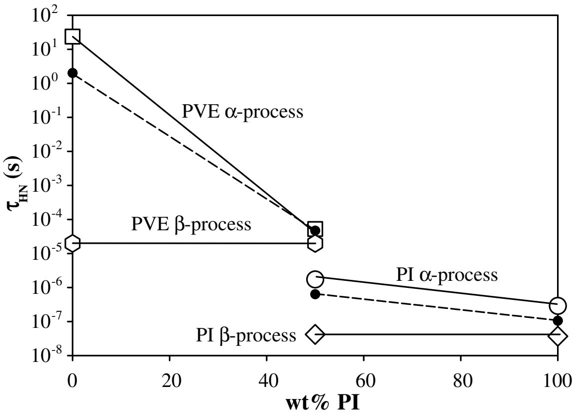

Fig. 7. The principal relaxation times for the pure melts (Eq. (1), also Table 1) and the blend (Eq. (2), also Table 1) obtained from our fits (open symbols) and extrapolation of 2D NMR results from Chung et al. [13] (filled symbols). The lines serve to guide the eye.

(2) The relaxation time for the α-relaxation process of the PVE component is strongly influence by blending (see Fig. 7). After blending, we obtain a difference of a factor of 30 between the α-relaxation times for the PVE and PI component, consistent with 2D NMR measurements [13] where extrapolation from lower temperatures yields a difference of around a factor of 70 (see Fig. 7). The correspondence of segmental relaxation times from 2D NMR studies and the α-relaxation times from dielectric measurements based on our analysis indicates that 2D NMR measurements [13] are sensitive primarily to the α-relaxation of the component polymers due to inability of this technique to access relaxations on time scales faster than a μs.

(3) The PVE α-relaxation process is observed to narrow and the PI α-relaxation process to broaden upon blending (see HN shape parameters in Table 1), consistent with our observations for the 50/50 CR-PBD/LB-PBD blend [12,21].

(4) The β-relaxation processes are essentially uninfluenced by blending. While this is an inherent assumption in our efforts to represent the dielectric loss of the blend (fixed shape, strength and relaxation time for the PVE component, fixed shape and strength for the PI component), the representation of the dielectric loss of the blend (Fig. 6) supports this assumption.

Unlike previous attempts to explain the behavior of PI/PVE blends, we do not find it necessary to invoke the concept of concentration fluctuations to account for the dynamically heterogeneous response of the blend as revealed by complex dielectric loss over a wide range of frequency. While the broadening of the α-relaxation process in the fast PI component in the 50/50 blend compared to the pure PI melt appears to be consistent with the concepts of the concentration fluctuation model, we in fact do not believe that concentration fluctuations play an important role in determining the dielectric response of the 50/50 PI/PVE blend at 270 K. The concentration fluctuation model predicts a maximum broadening of component relaxations for a 50/50 blend, while we observe monotonically increased broadening of the response of the fast (LB-PBD) component of our model CR-PBD/LB-PBD blend with increasing concentration of the slow CR-PBD component [12]. Furthermore, both the combined α- and β-relaxation process in the slow CR-PBD component of the LB-PBD/CR-PBD blends [12] and the α-relaxation of the slow PVE component of the PVE/PI blends appear to *narrow* upon blending with the fast (LB-PBD or PI) component, counter to the predictions of the CF model. Hence, while the cause of the broadening of the α-relaxation of the fast blend component (LB-PBD, PI) upon blending with the slow component (CR-PBD, PVE) is unknown, it does not appear to be due to local concentration fluctuations. One possible source of this broadening is a changing relationship between the cooperative α-relaxation, which is strongly influenced by the (ever slowing) environment upon blending with the slow component, and its precursor, the β-relaxation, which is not strongly influenced by blending and remains very strong.

The representation of the dielectric loss in the 50/50 blend as a sum of contributions from α- and β-relaxation process of the component polymers is better than can be obtained using the concentration fluctuation approach with a reasonable distribution of local environments [18] such as shown in Fig. 1, while an improved representation of the high-frequency loss in the context of concentration fluctuations requires an unphysically high probability of pure PI domains [25]. Most obviously, we can account for the significant high-frequency loss of the blend as being largely due to the β-relaxation of the PI component that does not shift with blending, as opposed to being due to a significant fraction of the PI α-relaxation that is not influenced by blending due to a PI-rich environment. The latter requires an unrealistically large fraction of PI to be surrounded by only PI segments. Secondly, neither our MD simulations of the 50/50 CR-PBD/LB-PBD blend nor our representation of the dielectric loss in the 50/50 PI/PVE blend at 270 K indicate significant broadening of relaxation processes that one would expect to accompany large local concentration fluctuations. On the contrary, both our simulation studies and our representation of experiment indicate a narrowing of the α-relaxation process in the dynamically slow component upon blending. In summary, we believe the apparent dynamically heterogeneous response of the 50/50 PI/PVE blend at 270 K is due to the very different response of the cooperative α-relaxation and local β-relaxation to blending and not to dynamically heterogeneous response induced by local compositional heterogeneities.

While we believe the reanalysis of the dielectric loss in a 50/50 PI/PVE blend presented here provides significant new insight into the dynamics of miscible polymer blends, it does not address some important issues. For example, while the relative magnitudes of the relaxation times for the relaxation processes in the 50/50 blend, i.e., τ_β (PI) < τ_α (PI) < τ_β (PVE) < τ_α (PVE) (see Fig. 7) are physically reasonable and are consistent with 2D NMR [13] and chain diffusion [24] measurements, neither our previously reported blend simulations nor the analysis of experimental data describe here allows us to predict these relaxation times based upon the behavior of the pure components. Secondly, our analyses of PI/PVE and CR-PBD/LB-PBD blends address the influence of blending on the β-relaxation in the dynamically fast component when that relaxation is due to mainchain polymer motions. How blending influences secondary processes that are due to side group motion is not considered in this representation and may be different than observed for the mainchain secondary process.

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