Anomalous Dynamical Homogeneity of the Dielectric α-Relaxation in Miscible Polymer Blends of Poly(epichlorohydrin) and Poly(vinyl methyl ether)

A. Alegría,* C. Elizetxea, I. Cendoya, and J. Colmenero

Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, E-20080 San Sebastián, Spain

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ABSTRACT: The dielectric α-relaxation of the poly(epichlorohydrin)/poly(vinyl methyl ether) miscible system is investigated in the frequency range 10^{-2}–10^{6} Hz. This polymer blend has the particularity that the components have nearly coincident glass-transition temperatures. We found that the relaxation spectra of these blends can be well described by the Kohlrausch–Williams–Watts law, the shape parameter being nearly temperature independent. This means that the dynamical heterogeneity commonly reported for the α-relaxation of miscible polymer blends is not found in this system. Our results suggest that the main reason for the dynamical homogeneity observed in the blend investigated in this work is that the neat components have nearly coincident T_g values. This can be considered as proof of the relevance of the difference between T_g of the blend components in the origin of the heterogeneous behavior commonly observed for the polymer blend dynamics in the α-relaxation range.

Introduction

The dynamics of miscible polymer blends has been a subject of increasing interest over the last years.[1–6] From a basic point of view, one of the most characteristic features of the dynamics of polymer blends is the strong difference between the segmental dynamics of polymer blends and those corresponding to their individual components. It is well known that the segmental dynamics, which is referred to as the α-relaxation, of conventional polymer melts show a series of universal characteristics such as the non-Debye character of the relaxation spectrum and the non-Arrhenius behavior of the temperature dependence of the characteristic time. The α-relaxation spectrum of a polymer melt can usually be well described by assuming a Kohlrausch–Williams–Watts form for the time decay of the relaxation function:

$$\Phi(t) = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

τ being the characteristic relaxation time and $0 < \beta < 1$ a parameter describing the non-Debye character ($\beta = 1$, Debye decay). In particular, eq 1 gives account of the asymmetric broadening of the α-relaxation toward the high-frequency side. Moreover, in conventional polymer melts, the temperature dependence of β, if it exists, is weak.[7] These dynamical characteristics of conventional polymer melts are usually referred to as dynamical homogeneity.

On the other hand, the α-relaxation of polymer blends also shows a strong non-Debye character. However, it is even broader and markedly more symmetric than that found for the neat components; i.e., it shows an important tail in the low-frequency side of the relaxation spectrum. In addition, contrary to conventional polymer melts, the relaxation shape is strongly temperature dependent. These features are considered as evidence that for polymer blends the α-relaxation process has a heterogeneous character whose origin is associated with the fluctuations of concentration present in polymer–polymer mixtures.[8] In this concern, two main theoretical approaches have been proposed.[3,6] Fischer and coworkers[6] based their approach on the fact that the fluctuations of concentration should give rise, through the T_g dependence on composition, to a distribution of relaxation processes. In this approach, it is assumed that the distributed processes have different time scales, being the relaxation shape of a given process observed in the corresponding component. Thus, in this framework, the relevant parameter controlling the segmental dynamics of a miscible blend is the difference between the characteristic relaxation rates of the polymer components, which is connected with the difference between the T_g values. The other approach[3] considers that the fluctuations of concentration produce different environments around the chain segments of a given component. On the basis of the coupling model (CM) scheme,[9] it is considered that these different environments induce a distribution of both the relaxation rate and the relaxation shape of the individual processes. In this approach, the difference between the coupling between the molecular units and their surroundings, which in the CM framework is directly connected with the relaxation shape, would play an important role.

Both approaches have been applied to describe the relaxation behavior of several polymer blend systems:[3,4,6,10] poly(vinyl methyl ether)/polystyrene, poly(vinylethylene)/polyisoprene, tetramethyl polycarbonate/polystyrene, tetramethyl polycarbonate/polycarbonate, and poly(cyclohexyl acrylate-*stat*-butyl methacrylate)/polystyrene, among others. A common feature of these systems is that the neat components show quite different glass-transition temperatures. However, up to now, no definitive conclusion about which model allows a better description of the experimental behavior has been found.

A significant number of results published about polymer blend segmental dynamics have been obtained by using the dielectric spectroscopy technique,[1,2,4,6] which has been demonstrated to be an adequate tool for studying this problem. In particular, if only one component is dielectrically active, the segmental dynamics of this single component in the blend can be investigated by means of dielectric techniques.[1] In other cases, the dielectric measurements have allowed detec-

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* To whom correspondence should be addressed.

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Table 1. Values of the Calorimetric Glass Transition Temperature T_g, the Dielectrically Defined T_{gD}, and Fitting Parameters Describing the $\tau(T)$ Behavior According to Eq (3)[a]

sample	T_g/K	D	T_0/K	T_{gD}/K	T_0*/K
PECH	247.5	5.71	206.8	249.6	206.3
PECH90/PVME10	248.4	5.68	207.0	250.6	207.1
PECH80/PVME20	248.8	5.37	211.0	251.5	207.9
PECH60/PVME40	250.8	5.81	208.5	252.4	208.6
PECH50/PVME50	251.4	5.68	209.5	252.5	208.7
PECH35/PVME65	250.8	5.55	210.2	252.2	208.4
PECH20/PVME80	250.0	5.78	207.7	251.2	207.6
PECH10/PVME90	249.1	5.90	206.8	251.2	207.6
PVME	246.8	5.91	205.8	249.9	206.6

[a] T_0* refers to T_0 values obtained by assuming a constant D value of 5.8.

tion of two separated relaxation processes in a miscible blend, each of them attributed to the dynamics of each component.[4]

In the present paper, we report a dielectric spectroscopy study of the α-relaxation on the polymer blend system poly(epichlorohydrin)/poly(vinyl methyl ether), which has recently been reported to form miscible blends.[11,12] The particular interest of this system is that these two polymers have a very similar glass-transition temperature. Despite the similarity in the glass-transition temperature, the dielectric relaxation of the neat polymers shows a markedly different shape. These features could help to establish whether the segmental dynamics of miscible polymer blends depends mainly on the difference between the T_g values of the neat components or it is also affected by the difference in the relaxation shapes. Moreover, the results obtained will give insight about the range of applicability of the models above-mentioned above.

Experimental Section

Blend components poly(epichlorohydrin) (PECH) and poly(vinyl methyl ether) (PVME) were obtained from Aldrich, Catalog numbers 18,186-2 and 18,272-9, respectively. Blends containing different weight fractions of PVME and PECH were prepared by dissolving the two components in THF and by casting from the solution at room temperature directly on the lower electrode. Films of the homopolymers were also prepared in the same way. The films were maintained for several days at 60 °C under vacuum conditions to completely remove the solvent. The thickness of the obtained films was about 0.05 mm. The blend films were transparent over the entire composition range, showing good mixing of the components. Calorimetric glass-transition temperatures T_g of the samples investigated were determined by means of a Perkin-Elmer DSC4 differential scanning calorimeter. In these measurements, sample weight was about 10 mg and T_g values (see Table 1) were calculated from the inflection point of the DSC scans at 10 K/min on samples previously cooled from 270 K at the same rate. The miscibility of this system has recently been established by means of both differential scanning calorimetry (DSC)[11] and ^{13}C and ^{129}Xe nuclear magnetic resonance.[12]

Dielectric measurements in the frequency range $10^{-2}-10^{6}$ Hz were performed following standard procedures. The experimental setup, which was supplied by Novocontrol GmbH, consisted of an SI 1260 Solartron-Schlumberger frequency response analyzer supplemented by a high-impedance preamplifier of variable gain. The sample was kept between two condenser plates (gold-plated electrodes) that were maintained at a fixed distance. Frequency scans were performed at constant temperatures. The temperature stability was better than 0.1 K. The temperature dependence of the dielectric losses at a fixed frequency of 10 Hz for the neat polymers is presented in Figure 1. In addition to the low-temperature secondary relaxations, both polymers display the main α-relaxation in the same temperature range, in agreement with their very close T_g values.

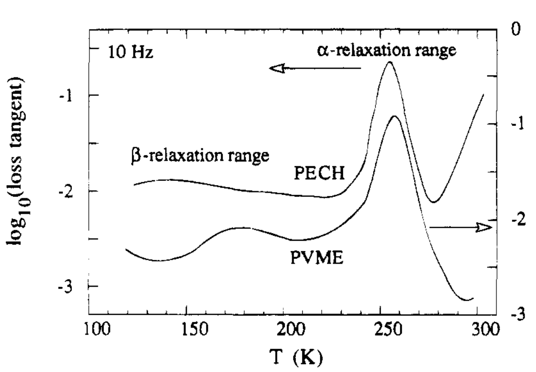

Figure 1. Dielectric losses of PECH and PVME at a fixed frequency of 10 Hz as a function of temperature.

Results

Since dielectric spectroscopy measures the frequency dependence of the complex dielectric permittivity $\epsilon^* = \epsilon' - i\,\epsilon''$ and the real and the imaginary parts contain the same dynamical information, only the ϵ'' results will be used in the further analysis. On the other hand, it should be pointed out that the secondary relaxations appearing in Figure 1 are also present in the blends. A preliminary analysis of these secondary relaxations showed that the responses of the blends correspond to the weighted superposition of the responses of the neat polymers; i.e., no clear effect of blending in the secondary relaxation processes was found. In this paper, we will focus our attention on the α-relaxation range.

Figure 2 shows the frequency dependence of ϵ'' in the T range where the segmental dynamics is active in the frequency window for several samples investigated. A first result we obtain from Figure 2 is that the curves corresponding to the neat polymers and those corresponding to the polymer blends display very similar features. This is opposite to the characteristics of the segmental behavior of previously investigated polymer blends. Neither a broadening in the low-frequency side nor an important change of the relaxation shape with temperature is observed in the PECH/PVME blends investigated.

A comparison among the frequency dependence of ϵ'' corresponding to all the samples investigated at a common temperature $T = 260$ K is presented in Figure 3a. In Figure 3b, the composition dependence of the frequency at the maximum of ϵ'', $f_{\max}$, and the full width at half-maximum (fwhm) of the relaxation peak at this temperature are shown. In addition to the difference in the relaxation strength, which follows the behavior expected from a simple addition of the relaxation strength coming from each component in the blend, two features are relevant in Figure 3. First, the relaxation rate decreases as the 50:50 composition is approached from both sides, indicating a slowing down of the relaxation process by blending. Second, the relaxation peak narrows continuously with composition from PECH to PVME, which shows the broader relaxation at this temperature. The former of these results seems to be related to the effect of composition in the glass transition temperature, which increases about 4 degrees for the 50:50 blend (see Table 1). The latter is a strong indication of the dynamical homogeneity of this polymer blend system, which is opposite to the dynamical heterogeneity commonly observed in the majority of the polymer blends investigated.[1-6,8,10]

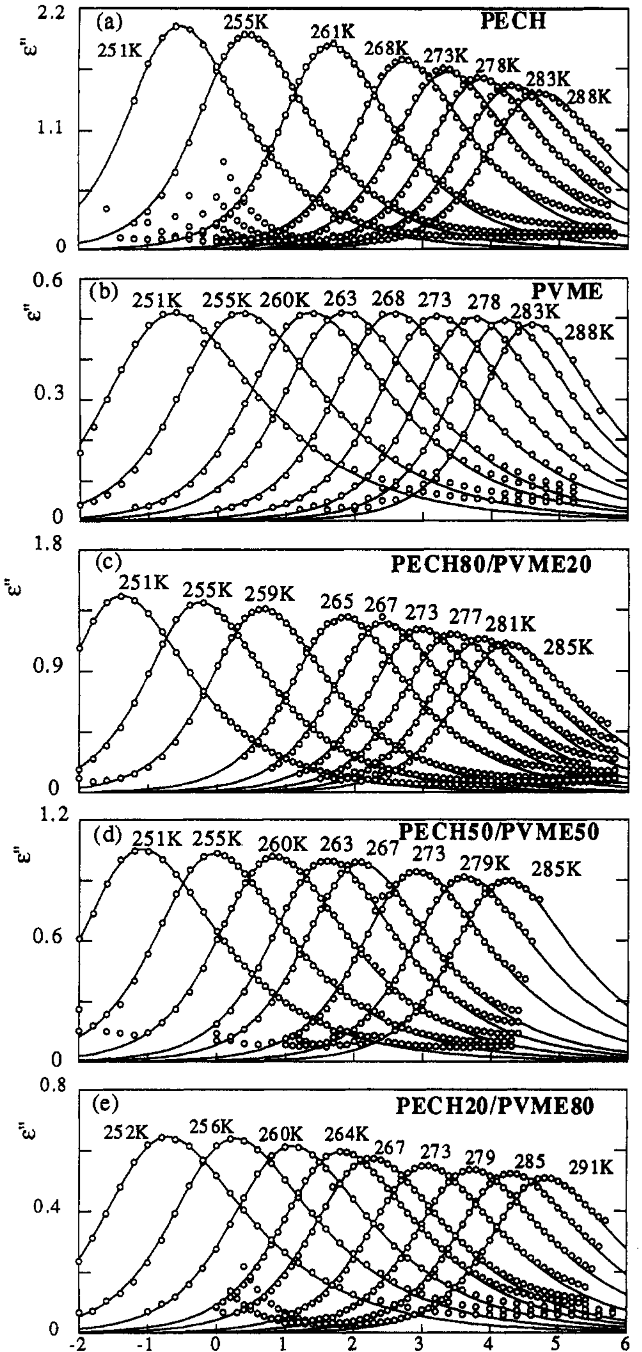

Figure 2. Isothermal dielectric losses of PECH (a), PVME (b), and several blends (c–e). Solid lines represent the fitting curves according with a KWW description.

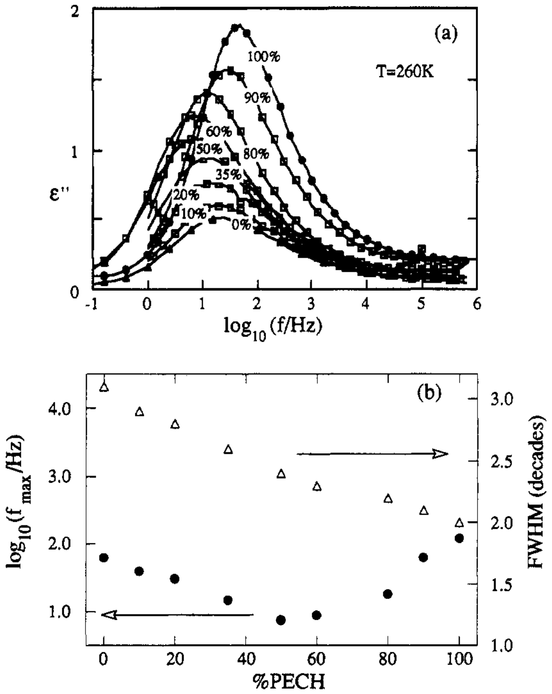

Figure 3. (a) Dielectric losses of all the samples investigated at 260 K (the lines are only a guide for the eye). The label indicates the weight fraction of PECH in each sample. (b) Composition dependence of the position f_{max} (●) and the width at half-maximum of the relaxation peak (△).

As a consequence of the particular dynamical behavior of this system, a KWW description of the segmental relaxation processes of the blends remains possible. Thus, the ϵ'' frequency behavior of all the samples investigated were fitted assuming a KWW form for the time decay of the relaxation function. The method of analysis used, which has been described elsewhere,[13] is based on a Havriliak–Negami (HN) equation.[14]

$$\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon\frac{1}{[1 + (i\omega\tau_{HN})^{\alpha}]^{\gamma}} \qquad (2a)$$

where ϵ_∞ is the unrelaxed value of the permittivity, $\Delta\epsilon$ is the relaxation strength, α and γ are two shape parameters in the range zero unity ($0 < \alpha,\gamma < 1$), and τ_{HN} is a characteristic relaxation time. Under the restriction

$$\gamma = 1 - 0.812(1 - \alpha)^{0.387} \qquad (2b)$$

eq 2a is a good approximation of the permittivity corresponding to a KWW time decay[15] with the following relation among the HN parameters and the ones corresponding to the KWW law

$$\beta = (\alpha\gamma)^{1/1.23};$$
$$\log \tau = \log \tau_{HN} - 2.6(1 - \beta)^{0.5} \exp(-3\beta) \qquad (2c)$$

By following this method, once the HN fitting parameters were obtained from the fitting procedure, eq 2c allowed calculation of the corresponding KWW parameters. Solid lines in Figure 2a–e stand for the fitting curves obtained. It is apparent that the KWW description is good enough to describe the main part of the relaxation peak although a systematic excess of the dielectric losses in the high-frequency tails is apparent. This loss excess, which is also apparent for the neat polymers, would be mainly associated with the influence of the secondary relaxation (see Figure 1). From those fittings, the KWW parameters τ and β have been obtained as a function of T (see Figure 4). The relaxation shape, which is characterized by the β parameter, has only a weak temperature dependence for all the samples (see Figure 4). Moreover, the values of β for the blends are intermediate to the ones of the neat polymers, in accordance with the behavior of the peak width shown in Figure 3b. Concerning the time scale of the segmental dynamics, we found that in spite of the nearly identical timescales of the segmental dynamics of the components, the values of τ for the blends are slightly larger than those found for the neat polymers (see Figure 4a), the main difference (of about one decade close to T_g) occurring around the 50:50 composition.

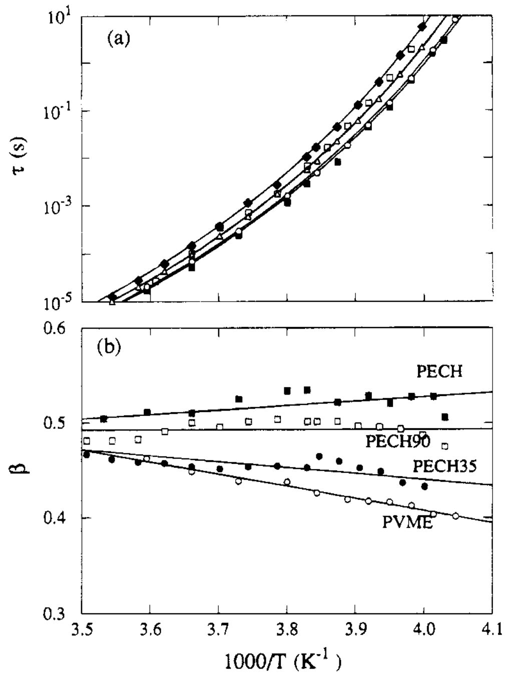

Figure 4. (a) Temperature dependence of the KWW relaxation time τ: (■) PECH; (□) PECH80; (◆) PECH50; (△) PECH20; (○) PVME. (b) β(T) behavior of the neat polymers and of two of the blends investigated.

The $\tau(T)$ behavior has been fitted by means of the usual Vogel–Fulcher (VF) equation:

$$\tau(T) = \tau_0 \exp\frac{DT_0}{T - T_0} \qquad (3)$$

where T_0 is a temperature below the experimental range at which the extrapolated relaxation time diverges, D is a parameter which can be related to the fragility concept first introduced by Angell,[16] and τ_0 is the reciprocal of an attempt frequency. In Figure 4a it is apparent that, when T increases, the values of $\tau(T)$ corresponding to the different samples seem to approach each other and eventually they merge into a single curve at very high temperatures. Thus, in the fitting procedure followed in this work, the prefactor of the VF equation has been fixed. In this way, the extra scattering among the parameters obtained from the different samples is reduced. Within the time scale covered, we found that the fitting of the $\tau(T)$ behavior is excellent for all the samples with $\tau_0 = 10^{-12}$ s. The values of the corresponding D and T_0 parameters are listed in Table 1. Moreover, from these VF fittings, it is possible to calculate the composition dependence of the dielectric glass-transition temperature, T_{gD}, defined as the temperature at which τ takes an arbitrarily fixed value, 1 s for instance. As can be seen in Table 1, the composition dependence of T_{gD} mirrors the composition dependence of the calorimetric glass transition temperature. Therefore, it seems that the difference in time scale among the segmental dynamics of the samples can be directly interpreted as a consequence of the differences of the glass-transition temperature.

On the other hand, from the values shown in Table 1, it is apparent that the values of D have no clear correlation with the blend composition, varying around an average value of $D^* = 5.8$. This fact has led us to test whether the $\tau(T)$ behavior can be described assuming this D^* value constant for the entire composition range, T_0 being the unique fitting parameter. We obtained a description of $\tau(T)$ which is still excellent. Moreover, the values of T_0 so obtained, which are referred to as T_0^*, are clearly correlated with the calorimetric T_g values (see Table 1), the difference $T_g - T_0^*$ being 41.2 ± 1 K; i.e., it is possible to write the following equation for $\tau(T)$:

$$\tau(T) = 10^{-12}\ \mathrm{s} \times \exp\frac{5.8(T_g - 41.2\ \mathrm{K})}{T - T_g - 41.2\ \mathrm{K}} \qquad (4)$$

which is able to describe the $\tau(T)$ behavior over the entire composition range. Solid lines through $\tau(T)$ data in Figure 4a represent the behavior obtained from eq 4.

Discussion

As mentioned above, the KWW law is able to describe the α-relaxation spectra of PECH/PVME polymer blends over the entire composition range. Moreover, the relaxation shape, which indeed has been characterized by the β parameter, has only a weak temperature dependence for all the blends. The values of β for the blends, and their temperature dependence as well, are intermediate to the ones of the components. All these results can be considered as a strong indication that in the PECH/PVME blend system the dynamical heterogeneity commonly observed in polymer blends is not present. This is a hard test, taking into account that the neat polymers are both dielectrically active. Thus, any small difference in the time scale of the corresponding segmental dynamics of each component should show up, at least, as an extra broadening of the relaxation peak, if not as a shoulder or a double peak feature as was recently found for the PVE/PIP system.[4] These possibilities should lead to a minimum in β as a function of concentration (a maximum in the peak width) rather than the monotonous variation observed experimentally.

On the other hand, the reduction in the relaxation rate observed in this system is opposite to previous results on other equal T_g component blends.[5] In that case, the segmental dynamics was found to be speeded up, which was attributed to a decreasing of density due to unfavorable mixing interactions between the components. Thus, the increase of T_g for the blends with respect to the T_g's of both components in the PVME/PECH system could by accounted for by assuming weak interactions favoring the mixing of the components. A more extended discussion of the different factors controlling the time scale dynamics in polymeric mixtures, which is not the objective of this work, can be found elsewhere.[5] Therefore, we now focus our attention on the fact that the PECH/PVME system displays an unusual dynamical homogeneity, which will be discussed in the framework of the preexisting models.

As commented above, two main approaches to explain the dynamical heterogeneity of polymer blends have been proposed. Fischer's approach[6] considers that the particular dynamical behavior of polymer blends is produced by a distribution of T_g values each of them associated with the different regions induced by the fluctuations in concentration, which, although having a dynamical character, have a lifetime much larger than the time scale of the segmental motions. In this framework, due to the nearly concentration-independent T_g values of the PVME/PECH system, the possible fluctuations in concentration do not induce a significant distribution of T_g. Taking into account the T_g values shown in Table 1, the distribution of T_g values would have a full width of about 4 K and, therefore, the distribution of τ values deduced through eq 5, a width lower than a decade. Such a distribution would produce a change in the relaxation shape parameters that is within the error bars estimated for this parameter. Therefore, the dynamical homogeneity found in this system is in perfect agreement with the predictions of this model.

The coupling model was developed for describing the dynamical behavior of complex correlated systems.[9] In addition to eq 1, this model allows one to establish a relationship between the so-called primitive process and the macroscopic (observed) relaxation. This relationship reads as

$$\tau = [\tau_p \omega_C{}^n (1 - n)]^{1/(1-n)} \tag{5}$$

where ω_c is a cutoff frequency that for polymers is estimated to be around 10^{11} s^{-1},[17] τ is the time characteristic of the observed relaxation (eq 1), τ_p is the time characteristic of the primitive (without intermolecular coupling) process, and n ($0 < n < 1$) characterizes the coupling between the motion of the relaxing unit and its environment ($n = 0$ when no coupling exists). In this scheme, the coupling index n is closely related to the β exponent of eq 1 ($\beta = 1 - n$). This framework has been used to account for the empirical correlation usually found between the value of β and the $\tau(T)$ behavior around T_g.[18]

Equation 5 has been applied to different types of complex systems such as glass-forming liquids, polymers, and polymer blends, among others.[10,19] Following this scheme, the coupling model approach to the segmental dynamics of miscible polymer blends assumes that the fluctuations in concentration occur at the molecular level. Therefore, each segment in the blend is surrounded by different environments inducing changes in the coupling parameter. Thus, in conventional polymer blends where the components have very different T_g's, in the CM framework it is expected that the coupling between the motion of the structural unit and its surroundings is affected by the fluctuations of concentration, n therefore being distributed between the values corresponding to the neat polymers forming the blend. Moreover, taking into account that τ_p is assumed to be independent of blending, the distribution of n leads, through eq 5, to a distribution of macroscopic relaxation times τ, which explains the dynamical heterogeneity of polymer blends. However, for blends where the components have similar T_g's, the CM is not able to make predictions about the blend dynamics.[10] In these cases, additional knowledge of the potential and steric interactions between respective chemical groups is required since the chain segments of the two components relax with very similar time scales. Taking into account that the values of n of both components are different, $n \cong 0.47$ for PECH and $n \cong 0.60$ for PVME, a naive application of the CM ideas to the system investigated would lead to a dynamic heterogeneity opposite to our experimental findings. However, because of the aforementioned reasons, a rigorous test of this model is not possible in the PECH/PVME system.

Conclusions

In summary, we have shown that the dynamical heterogeneity commonly reported for the α-relaxation of miscible polymer blends is not found for the PECH/PVME system. Our results suggest that the main reason for this is that we are dealing with a system formed by neat polymers with nearly coincident T_g values. Therefore, the difference between T_g of the blend components appears to be the relevant feature giving rise to the heterogeneous behavior of polymer blend dynamics in the α-relaxation range.

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