

Describing the component dynamics in miscible polymer blends: Towards a fully predictive model

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We have recently proposed [D. Cangialosi *et al.*, *J. Chem. Phys.* **123**, 144908 (2005)] an extension of the Adam-Gibbs [*J. Chem. Phys.* **43**, 139 (1965)] theory, combined with the concept of self-concentration, to describe the temperature dependence of the relaxation time for the component segmental dynamics in miscible polymer blends. Thus, we were able to obtain the dynamics of each component in the blend starting from the knowledge of the dynamic and thermodynamic data of the pure polymers, with a single fitting parameter (α) which had to be obtained from the fitting of the experimental data. In the present work we demonstrate that this model is also suitable to describe the polymer segmental dynamics in concentrated polymer solutions. From this result we have developed a new route for determining the value of the α parameter associated with any given polymer. Once this value is known for the two components of a possible polymer blend, our model for polymer blends dynamics becomes fully predictive. © 2006 American Institute of Physics.

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INTRODUCTION

Understanding how the segmental dynamics of a polymer is affected by blending with another component has been recently a challenge involving a great deal of scientific research.¹⁻⁶ This problem has a clear relevance from a technological as well as basic point of view. In the first case, by blending two polymers it is possible to obtain new materials whose properties will be controlled by those of the pure components. To predict the properties of a given blend is of obvious practical utility and allows tuning the characteristics of the final material. From a basic point of view, the dynamics of miscible polymer blends displays peculiar features that make the study of these systems very attractive. In particular, the presence of a component in the environment relevant for the segmental dynamics of a polymer possessing a relatively different dynamics implies a slowing down or a speedup of the dynamics depending on the nature of the other component. The effect of the other component is strongly related to the length scale involved in the segmental dynamics. This has been highlighted by Lodge and McLeish (LM),⁷ who introduced the concept of effective concentration, i.e., the concentration in the volume relevant for segmental dynamics.

We have recently presented a model,⁸ based on the combination of the self-concentration concept⁷ and the Adam and

Gibbs (AG) theory,⁹ which describes the component dynamics in miscible polymer blends. In particular, we make use of both the relation between the relaxation time and the configurational entropy and the concept of the increasing length scale with decreasing temperature implicit in the AG theory. We showed that once the dynamics and the thermodynamics of the pure components of the blends are known, the dynamics of a given component in a miscible polymer blend is well described by our model through just one fitting parameter (α) relating the relevant length scale for dynamics to the configurational entropy. The fact that this parameter has to be obtained from the experimental data of the blend and cannot be obtained from the pure components makes our model not completely predictive.

In this work we studied the dynamics of poly(vinyl methyl ether) (PVME) in concentrated solutions with a low molecular weight glass former (toluene) and in two polymer blends, polystyrene (PS) and poly(*o*-chloro styrene) (PoClS). We found that the results for the polymer/solvent mixtures can be analyzed according to the proposed model, mainly in concentrate solutions, and the value of α can be obtained at different concentrations. We show here that a simple extrapolation of the so obtained parameter values to 100% PVME allows us to determine the α value needed to describe the PVME segmental dynamics in the two polymer blends here investigated. Thus, by tabulating the value of α for the different polymers, our model would become completely predictive.

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THEORY

In a previous work⁸ we provided a new approach to describe the component segmental dynamics of miscible polymer blends combining the concept of chain connectivity and the Adam-Gibbs theory. A full and detailed description of such approach can be found in Ref. 8 and just a brief summary will be presented here, in order to understand the role of the parameter α and its relevance to make the model fully predictive.

The AG theory assumes that the decrease of the available configurations upon temperature reduction is the cause of the non-Arrhenius slowing down of the segmental dynamics. Based on this hypothesis, they proposed that the segmental relaxation time can be related with the configurational entropy through⁹ $\tau = \tau_o \exp(\Delta\mu s_c^*/k_B T S_c) = \tau_o \exp(C/T S_c)$ where k_B is the Boltzmann constant, S_c is the configurational entropy, $\Delta\mu$ is the energy barrier per particle over which a cooperatively rearranging group must pass, s_c^* is the configurational entropy associated with such a rearrangement, and τ_o is the relaxation time at infinite temperature. Thus, we write the relaxation time of the component A in the blend according to

$$\tau^{A/\text{blend}} = \tau_o \exp\left[\frac{C^{A/\text{blend}}}{T S_C^{A/\text{blend}}}\right], \quad (1)$$

which is only valid when both components are in thermal equilibrium. Here $C^{A/\text{blend}}$ and $S_C^{A/\text{blend}}$ are a material constant and the configurational entropy for polymer A in the blend, respectively. A similar equation can be written for component B . The value of τ_o was assumed equal to that of the pure polymer since it represents the relaxation time at high temperatures where the dynamics of both polymers are completely decoupled. $C^{A/\text{blend}}$ and $S_C^{A/\text{blend}}$ can be written as a linear combination of those corresponding to the pure polymers; thus

$$S_C^{A/\text{blend}} = \phi_{\text{eff}}^A S_C^A + (1 - \phi_{\text{eff}}^A) S_C^B, \quad (2a)$$

$$C^{A/\text{blend}} = \phi_{\text{eff}}^A C^A + (1 - \phi_{\text{eff}}^A) C^B, \quad (2b)$$

where ϕ_{eff} ($\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi$) is the effective concentration, which can significantly deviate from the macroscopic concentration, ϕ , depending on the value of the self-concentration (ϕ_s) which can be calculated as¹⁰

$$\phi_s = \frac{3l_k l_l}{2\pi r_c^2}, \quad r_c \leq l_k, \quad (3a)$$

$$\phi_s = \frac{3l_p}{2\pi r_c}, \quad r_c > l_k, \quad (3b)$$

where l_p and l_k are the packing and Kuhn lengths, respectively, and r_c is the radius of the relevant volume where the segmental relaxation takes place.

On the other hand, from the AG theory we know that the number of basic structural units (z^*) within a cooperatively rearranging region (CRR), whose size is predicted to increase upon temperature reduction, is inversely proportional

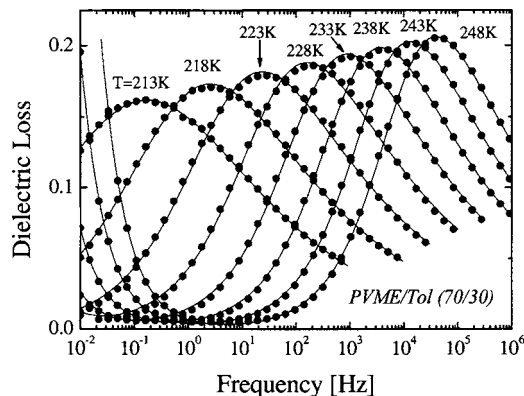


FIG. 1. Dielectric relaxation curves for PVME/toluene (70/30) at the indicated temperatures. The filled symbols represent the experimental data, whereas the solid lines are the fitting curves.

to the configurational entropy, $z^* \propto S_c^{-1}$, and therefore the size of such a CRR would be related to the configurational entropy by

$$r_c = \alpha S_c^{-1/3}, \quad (4)$$

where α is a proportionality constant which can be obtained from the fitting of the experimental data; i.e., from the data of the component dynamics in the blend. However, since S_c is experimentally inaccessible, we have assumed that the S_c is proportional to the excess entropy (S_{ex}). Although this point is still a matter of open debate, several studies seem to support this hypothesis.^{11–13} Thus the excess entropy can be calculated from calorimetric measurements as

$$S_{\text{ex}}(T) = \int_{T_K}^T \frac{\Delta C_p(T')}{T'} dT', \quad (5)$$

where $\Delta C_p = C_p^{\text{melt}} - C_p^{\text{glass}}$ is the excess heat capacity and T_K is the Kauzmann temperature where the excess entropy tends to vanish.

This system of equations [Eqs. (1)–(5)] can be exactly solved and gives an excellent description of the component dynamics of each polymer in the blend at any concentration and temperature, once the parameter α is determined from the experimental data.⁸

EXPERIMENT

Dielectric measurements on mixtures of poly(vinyl methyl ether)/toluene (PVME/tol), at different concentrations between 50 and 88% (w/w) of PVME, were carried out by means of an Alpha analyzer (Novocontrol GmbH) in the frequency range of 10^{-2} – 10^6 Hz. The dielectric measurements were performed by frequency sweeps at constant temperature, with stability better than ± 0.1 K. Figure 1 shows the dielectric loss (ϵ'') for PVME/tol (70/30) as a function of frequency at different temperatures. From the so obtained spectra, the main peak, i.e., the alpha relaxation, was fitted with the Havriliak-Negami (HN) function $\epsilon^*(\omega) - \epsilon_\infty = \Delta\epsilon [1 + (i\omega\tau_{\text{HN}})^\alpha]^{-\beta}$ where $\Delta\epsilon$ is the relaxation strength, τ_{HN} is a relaxation time, and α and β are shape parameters. To the purpose of this work, the characteristic relaxation time will be that of maximal loss $\tau = \tau_{\text{max}} (\tau_{\text{max}} = \tau_{\text{HN}} (\sin(\alpha\pi/2$

TABLE I. Relevant parameter for the here studied components. Errors are ± 1 of the least significant digit.

| Component | T_g (K) | Thermodynamics parameters | | Dynamics parameters | | | Structural parameters ^a | |
|--------------------|-----------|--|--|---------------------|--------------|-----------|------------------------------------|------------------|
| | | a (J K ⁻¹ mol ⁻¹) | b (J K ⁻¹ mol ⁻¹) | $\log(\tau_0$ (s)) | C (kJ/mol) | T_K (K) | l_k (Å) | l_p (Å) |
| Toluene | 117 | 105.0 | -0.310 | -14.7 | 58.3 | 95.9 | ... | ... |
| PVME ^b | 249 | 68.3 | -0.160 | -13.0 | 51.6 | 203.4 | 13 | 2.7 |
| PS ^b | 373 | 99.0 | -0.171 | -12.4 | 60.7 | 322.2 | 18 | 3.9 |
| PoCIS ^b | 402 | 98.4 | -0.172 | -12.9 | 61.8 | 340.6 | 17.3 | 3.9 ^c |

^aAll parameters were taken from Ref. 10 except the Kuhn length of PoCIS that was taken from Ref. 20.

^bData for pure polymers were taken from Ref. 8.

^cThe packing length of PoCIS was assumed equal to that of PS due to the lack of published data.

$+2\beta))^{-1/\beta}(\sin(\alpha\beta\pi/(2+2\beta))^{1/\beta})$.¹⁴ Thus, we obtained the temperature dependence of the relaxation time for the PVME/tol mixtures at the different concentrations. Dynamics data of pure toluene were taken from Ref. 15, whereas the temperature dependence of the relaxation times for PVME, PS, and PoCIS was taken from Ref. 8.

RESULTS AND DISCUSSION

PVME dynamics in concentrate solutions

As aforementioned, we need to know $\Delta C_p = C_p^{\text{melt}} - C_p^{\text{glass}}$ as a function of the temperature for each component in order to estimate its excess entropy. We showed⁸ that the heat capacity can be well described by a linear function both above and below T_g . Thus, the excess heat capacity (ΔC_p) can be expressed according to the empirical linear equation $\Delta C_p = a + bT$, which is recognized to be the most accurate form.¹⁶ Calorimetric data for PVME, PS, and PoCIS were taken from Ref. 8 whereas heat capacity data for toluene were taken from Ref. 17. Table I shows the corresponding values of a and b for the three polymers and for toluene. Once ΔC_p is known we can replace it in Eq. (5) and integrate it to obtain the following expression for the excess entropy:

$$S_{\text{ex}}(T) = a \ln(T/T_K) + b(T - T_K). \quad (6)$$

Thus, it is possible to fit pure component dynamics data by means of the AG equation

$$\tau = \tau_0 \exp\left(\frac{C}{TS_{\text{ex}}}\right) = \tau_0 \exp\left(\frac{C}{T(a \ln(T/T_K) + b(T - T_K))}\right). \quad (7)$$

Equation (7) gives an excellent fit of the experimental dynamics data of pure components, as shown in Figs. 2 and 4 for PVME. The resulting fitting parameters (τ_0 , C , and T_K) for all pure components are listed in Table I. This table also shows the values of the Kuhn and packing lengths for all pure polymers. These values are used to relate the relevant volume for segmental relaxation with the self-concentration by means of Eq. (3).

Once the dynamics and thermodynamics of the pure components are known we can use the proposed model to fit the experimental dynamics data at different concentrations. Figure 2 shows the dielectric relaxation time versus temperature for mixtures of PVME with toluene at the indicated compositions. The continuous lines are the best fitting of the

model to the experimental data. The best-fitting values of α are shown in Fig. 3. It is interesting to note that contrary to what occurs for polymer/polymer blends,⁸ α changes significantly with concentration when PVME is mixed with toluene. This is probably due to the fact that we are probing the segmental dynamics at long time scales compared to PVME/polymer blends. According to the AG theory, the increase of the relaxation time is associated with an increase of the cooperative volume and therefore the relevant volume for dynamics is large enough to include a large amount of the other component (toluene). This suggests that the value of α for pure toluene could be significantly larger than the corresponding one for pure polymers. In fact, the data on Fig. 3 suggest the possibility of using an empirical mixing rule for the value of α ($\alpha^{A/\text{blend}} = \phi_{\text{eff}}^A \alpha^A + (1 - \phi_{\text{eff}}^A) \alpha^B$) when polymer/solvent mixtures are analyzed. However, this was not necessary for polymer blends considered so far where the value of α is expected to vary very slightly with composition according to previous results.⁸

It is also worth noticing that although the fitting is excellent for those data points corresponding to samples with high PVME contents ($\geq 70\%$), some systematic deviations between the prediction and the experimental data start appearing at lower PVME contents. This is not unexpected because the model was developed for athermal polymer

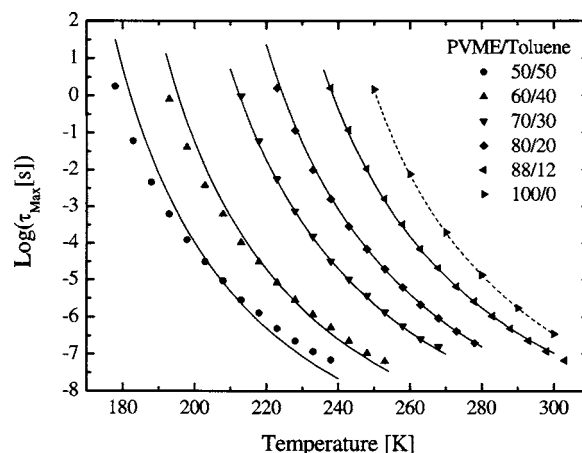


FIG. 2. Relaxation times as a function of temperature for PVME/toluene mixtures at the indicated concentrations. The dashed line represents the best fit of the pure PVME experimental data (triangles right) by means of Eq. (7). The corresponding values of τ_0 , C , and T_K are listed in Table I. The filled lines are the best fit of the proposed model to the experimental data.

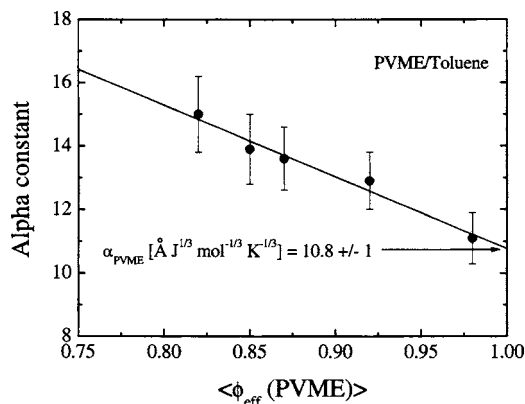


FIG. 3. Alpha parameter vs PVME effective concentration for PVME/toluene mixtures. The solid line represents the best linear fit and extrapolates to $\alpha = (10.8 \pm 1) \text{\AA}^3 \text{J}^{1/3} \text{mol}^{-1/3} \text{K}^{-1/3}$ for pure PVME.

blends and we have, for low PVME contents, something more similar to a dilute polymer solution. Additionally, relevant hydrodynamics and interaction effects could appear for high solvent contents and therefore the model would no longer be valid in the present form. On the other hand, at high polymer concentrations hydrodynamics effects are screened and any interaction term between both components tends to vanish and therefore the assumption of athermal mixtures is still a good approximation. Thus, the model developed for polymer blend dynamics works very well on the rich PVME (i.e., polymer) side of solutions. This indicates that this model is also suitable to analyze not only polymer solutions but also, for instance, how plasticizers affect the segmental dynamics of the polymers they are mixed with when they are present in relative small quantities (up to 20% or 30%).

Figure 3 shows that the extrapolation to an effective concentration of one (pure PVME) allows us to estimate the value of the constant α for PVME. The solid line in Fig. 3 represents the best linear fit to the calculated values of α for PVME/tol mixtures. A value of alpha [$\alpha = (10.8 \pm 1) \text{\AA}^3 \text{J}^{1/3} \text{mol}^{-1/3} \text{K}^{-1/3}$] was obtained for pure PVME. Thus, by tabulating the value of α for each polymer we can establish a method to have a fully predictive model to describe the component dynamics in a polymer blend, once the dynamics and thermodynamics of the pure components are known. This will be confirmed in the following, where we will see how using the obtained value of alpha we are able to describe the component dynamics of PVME in two different polymer blends.

PVME dynamics in polymer blends

Figures 4(a) and 4(b) show the relaxation times as a function of the temperature for PVME in blends with PS and PoCIS, respectively, at the indicated concentrations, taken from Ref. 8. The fastest process in each figure represents the relaxation time of the pure PVME used above. The values of τ_o , C , and T_K for the pure polymers are listed in Table I.

Once the parameters for the pure polymers are known, we can introduce in the model the calculated value of the alpha parameter, obtained from the solutions, to predict the

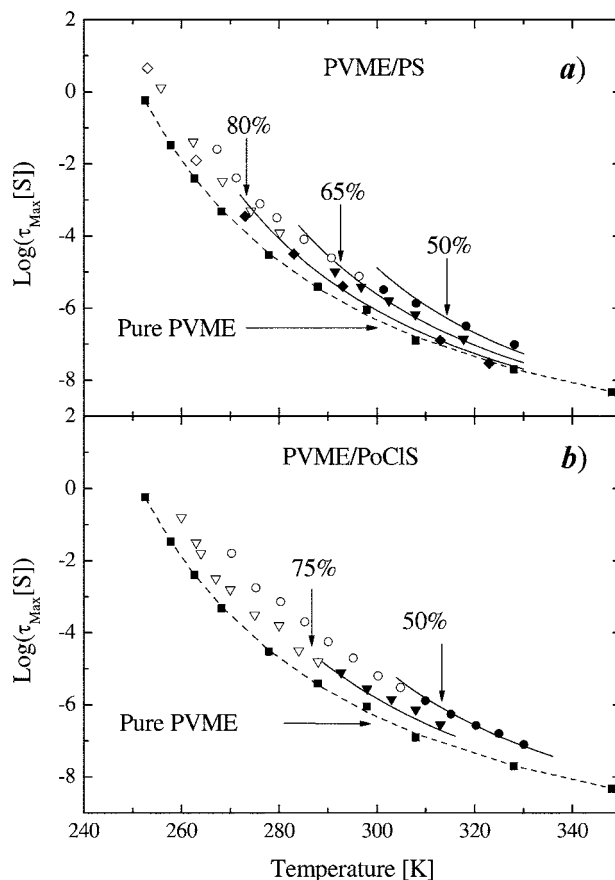


FIG. 4. (a) Experimental relaxation times as a function of temperature for pure PVME (filled squares), PVME/PS 80/20 (diamonds), PVME/PS 65/35 (triangles), and PVME/PS 50/50 (circles). The filled symbols indicate that the system is in equilibrium and therefore the proposed model is valid to predict the experimental data. The solid lines represent the dynamics of PVME in PS predicted by the model. The dashed line represents the best fit of the pure PVME experimental data by means of Eq. (7). The corresponding values of τ_o , C , and T_K are listed in Table I. (b) Experimental relaxation times as a function of temperature for pure PVME (filled squares), PVME/PoCIS 75/25 (triangles), and PVME/PoCIS 50/50 (circles). The filled symbols and solid and dashed lines represent the same as in part (a).

temperature dependence of the relaxation times for PVME in the polymer blends. However, since PVME is the low T_g component in these two polymer blends, some nonequilibrium effects will appear¹⁸ as temperature is decreased and enters in the glass transition region of the blend. In this temperature range the high T_g component starts freezing and becomes rigid, confining the low T_g component.¹⁹ Hence, the system is no longer in equilibrium and the model cannot be applied in the present form. At higher temperatures, the system is in thermal equilibrium [filled symbols in Figs. 4(a) and 4(b)] and our approach should therefore be suitable. The temperature at which the system falls out of equilibrium can be identified from the differential scanning calorimetry (DSC) traces with the point where, by decreasing the temperature, the temperature derivative of the liquid heat capacity starts increasing due to the onset of the glass transition. For the PVME/PoCIS blends we found temperatures about 312 and 295 K for those with 50% and 75% of PVME, respectively; whereas for blends of PVME/PS this temperature is about 300, 284, and 270 K for concentrations of 50%, 65%, and 80% of PVME, respectively.^{18,20} The solid lines in

Figs. 4(a) and 4(b) represent the prediction of the model for the dynamics of PVME, over the appropriated temperature range, when it is blended with PS and PoCIS, respectively. It is clear from these figures that these predictions are in very good agreement with the experimental data.

CONCLUSIONS

We have used a recently proposed model, based on the AG theory and the self-concentration concept, to analyze the component segmental dynamics of PVME in different environments. From this analysis we showed that the model can also be applied to concentrated polymer solutions. This implies that the only fitting parameter (α) of our model for polymer blend dynamics can be calculated for the pure components from the extrapolation of those obtained for polymer/solvent mixtures at different concentrations. This fact not only establishes a method to determine the alpha parameter for the different polymers but also would make our model for polymer blend dynamics completely predictive. Therefore, the proposed approach would be now suitable to predict the component dynamics in a polymer blend once the dynamics, thermodynamics, and the alpha parameter of the pure components are known.

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