Notes

Modeling the Dynamics of Head-to-Head Polypropylene in Blends with Polyisobutylene

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Received October 11, 2005
Revised Manuscript Received October 25, 2005

The dynamics of miscible polymer blends has been the subject of intense research in recent years. This is due to the complexity of the dynamic response, which, among other features, manifests with the presence of two distinct segmental dynamics.[1,2] This has been mainly attributed to self-concentration effects as first proposed by Chung et al.[3] and later developed by Lodge and McLeish.[4] In other words, because of the relatively localized nature of segmental dynamics and the effect of chain connectivity, the effective concentration in the volume relevant for segmental relaxation is always different from the macroscopic concentration. Because of the fact that the volume probed by selective techniques can be centered on monomers of each component type, two segmental dynamics usually show up in the relaxation pattern of the blend. Apart from the now widely accepted role of self-concentration, the approach proposed by Lodge and McLeish (LM) makes use of a temperature-independent length scale of the order of the Kuhn segment to describe the average blend components dynamics. Despite the success of this approach in predicting the dynamics for a number of blends,[5] several recent papers suggest that an increasing length scale with decreasing temperature can produce a potentially more satisfactory fit of experimental data.[6,7] Moreover, a very recent study on the dynamics of head-to-head polypropylene/polyisobutylene (hhPP/PIB 30/70 wt %) blend seems to demonstrate the inability of a temperature-independent length scale to describe the segmental relaxation of hhPP in this blend.[8] The aim of this work is to show how a model recently presented by us[7] is able to predict hhPP segmental dynamics in PIB. This model is based on the combination of the self-concentration concept with the Adam−Gibbs (AG) approach to the glass transition. Apart from the correlation between the relaxation time and the configurational entropy, the model also makes use of the concept of the increasing length scale for segmental relaxation with decreasing temperature implicit in the AG theory.[9]

The application of the AG model to the dynamics of polymer blends relies on the evaluation of the configurational entropy and of the parameter C of the AG equation[9] as a function of the effective concentration to calculate the component relaxation time as

$$\tau = \tau_0 \exp\left(\frac{C(\phi_{\text{eff}})}{TS_{\text{ex}}(\phi_{\text{eff}})}\right) \tag{1}$$

Here the configurational entropy, experimentally inaccessible, has been replaced by S_{ex}, i.e., the entropy of the supercooled liquid in excess to that of the corresponding crystal. C and S_{ex} are calculated as a linear combination of the same properties of the pure components through the effective concentration in the volume relevant for dynamics.[7] The effective concentration, i.e., the concentration experienced by the relevant volume for segmental relaxation, is related to the self-concentration by[4] $\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi$, where ϕ_{eff}, ϕ_s, and ϕ are respectively the effective, the self-, and the macroscopic concentrations. The preexponential factor τ_0 in eq 1 is assumed to be concentration independent, being representative of the high-temperature behavior, where, as will be discussed later, the relevant volume for segmental dynamics approaches a size where intramolecular potentials dominate the dynamics.

It is noteworthy that according to our approach the excess entropy of a polymer is modified by the presence of the other, and this implies a slowing-down or a speeding-up of the dynamics depending on the mobility of the other component. The change of excess entropy and its associated dynamics upon blending has been recently investigated at a molecular level by solid-state NMR.[10,11] These studies nicely evidence the change of the dynamics upon blending analyzing the 2D exchange pattern of pure PIB and the same polymer in blends with polyethylene-*co*-butene for time scales much larger than previously achieved in NMR.

In addition, according to the AG model, the relevant length scale for segmental dynamics increases with decreasing temperature as a result of the decrease in the configurational entropy. This length scale is related to S_{ex} by

$$r_c = \alpha S_{\text{ex}}^{-1/3} \tag{2}$$

where r_c is the radius of the relevant volume for segmental relaxation and α is a polymer specific parameter assumed to be temperature independent. α can be evaluated through the fitting of experimental data exploiting the correlation between r_c and ϕ_s. This can be obtained through simple geometric considerations involving the packing and the Kuhn lengths.[6] More details on how the AG model is applied to the components dynamics of miscible blends can be found in ref 7.

To apply the aforementioned model, both the dynamic and thermodynamic parameters of the pure components of the blend have to be determined. In particular, the excess entropy of the pure components has to be calculated. In our approach, a linear form of the excess specific heat, $\Delta C_P = C_P^{\text{melt}} - C_P^{\text{crystal}} = a + bT$, where a and b are constants, was integrated to obtain the excess entropy. PIB specific heat was taken from the ATHAS

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10.1021/ma052197r CCC: $33.50
Published on Web 11/19/2005

Table 1. Dynamic, Thermodynamic, and Structural Parameters for hhPP and PIB

		dynamics parameters[a]			thermodynamic parameters[a]		structural parameters[a]	
polymer	T_g [K]	log(τ_0 [s])	C [kJ/mol]	T_K [K]	a [J/(K mol)]	b [J/(K^2 mol)]	l_k (Å)	l_p (Å)
hhPP	253	−11.3	11.0	195	4.9	0.043	25	3
PIB	200	−13.3	31.2	135	44.6	−0.106		

[a] Errors are ±1 of the least significant digit unless specified.

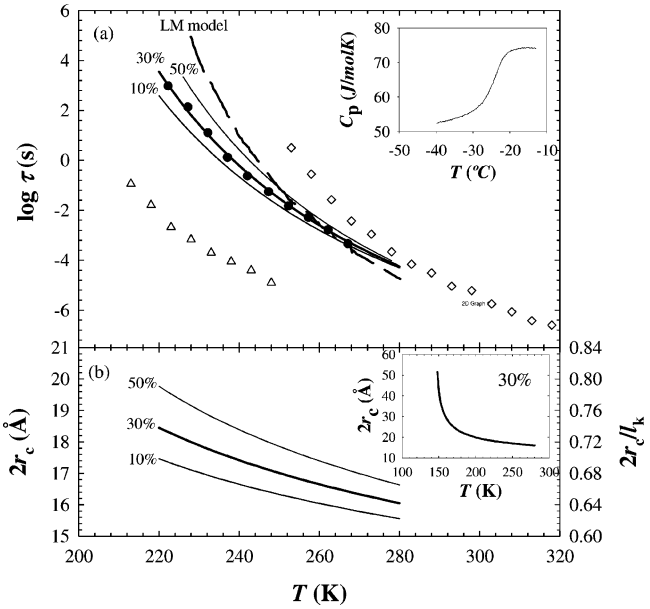

Figure 1. (a) Relaxation time vs temperature for hhPP in blend with PIB with 30% hhPP (filled circles), pure hhPP (empty diamonds), and pure PIB (empty triangles). All data are taken from ref 8. The thick solid line is the prediction of our model of hhPP segmental dynamics in blend with PIB, and the dashed line is the prediction of the LM model taken from ref 8. The thin solid lines are the prediction of our model for hhPP dynamics in blends with 10 and 50% hhPP. The inset shows the specific heat−temperature trace for pure hhPP obtained as described in the text. (b) Temperature dependence of the diameter (left axis) and its ratio with the Kuhn length (right axis) of the relevant volume for segmental relaxation for hhPP in blends with 30% (thick line) and 10 and 50% (thin lines). The inset shows the same plot for the blend with 30% hhPP but extended to lower temperatures than the ones experimentally accessible.

database where data for the crystal are also available.[12] To obtain a and b, for hhPP we have approximated the specific heat of the crystal with the one of the glass and extrapolated the latter above T_g. The specific heat of hhPP was determined by us through the differential scanning calorimeter (DSC-Q1000) from TA Instruments in temperature-modulated mode with an average heating rate of 0.1 K/min and amplitude of 0.3 K. Different oscillation frequencies were investigated, and the so-obtained specific heats were extrapolated to zero frequency to obtain quasi-static values. The inset of Figure 1 shows the quasi-static specific heat vs temperature plot for pure hhPP. Segmental dynamics data for pure hhPP and PIB were taken from ref 8 and fitted through the AG equation to obtain the preexponential factor, the parameter C, and the temperature where the relaxation time tends to diverge, identified as T_K, i.e., the temperature where S_{ex} related to the segmental relaxation extrapolates to zero.[15] All parameters (a, b, τ_0, C, and T_K) for hhPP and PIB are listed in Table 1. In this table, we also list the values of the Kuhn and packing lengths of hhPP taken respectively from refs 8 and 13.

Figure 1a shows the average relaxation time, as obtained by Krygier et al. for hhPP in a blend with 30% hhPP and 70% PIB.[8] The average relaxation times of pure hhPP and PIB are also shown in the figure. The thick solid line is the best fitting of the proposed model to experimental data. As can be observed, an excellent fitting is obtained, unlike the best LM description according to ref 8 and obtained with a value of the self-concentration of 0.75 (dashed line). The resulting value of the only unknown parameter of our model was $\alpha = 16.5$ Å J$^{1/3}$ mol$^{-1/3}$ K$^{-1/3}$. This value is comparable to that of other polymers in other miscible blends[7] and allows calculating the relevant length scale for segmental dynamics of 30% hhPP in PIB. As shown in Figure 1b, a length scale between 1.6 and 1.85 nm is obtained depending on the temperature. The obtained length scale is of the order of the hhPP Kuhn segment (2.5 nm). However, it is worth noting that the length scale obtained corresponding to the self-concentration value employed in ref 8 using the LM model turns to be smaller than the Kuhn segment and the length scale obtained by us. Apart from the possible differences arising from the assumption of a cube instead of a sphere as the appropriate shape of the relevant volume and the inaccuracy of the Fox equation to calculate the Vogel temperature,[14] the large value of the self-concentration required by the LM approach can be considered as a clear indication of the inability of a temperature-independent length scale to describe hhPP segmental dynamics in PIB in a wide temperature range.

Apart from the description of dynamics data already obtained, it is noteworthy that our model is able to predict the segmental dynamics of hhPP in PIB at different concentrations. This is due to the fact that the only fitting parameter of our model (α) has been shown to be polymer specific and, at least in polymer blends, roughly composition independent.[7] In Figure 1, we report as an example the predicted segmental dynamics of hhPP in PIB with 10 and 50 wt % hhPP and the corresponding length scale (thin solid lines).

Finally, we would like to remark that the accuracy of the LM model in describing dynamics data well above T_g[5,16] is compatible with the idea of a temperature-dependent length scale related to the configurational entropy. This is due to the fact when the AG theory is applied far above the Kauzmann temperature, i.e., the temperature where the configurational entropy is predicted to go to zero, the temperature variation of the configurational entropy becomes very smooth, resulting in a very weak temperature dependence of the relevant length scale for segmental dynamics. This high-temperature range is usually covered by neutron scattering techniques[16] and nuclear magnetic resonance.[5] This can explain why the data obtained by these techniques are often well described by the LM model with a temperature-independent length scale. On the other hand, here we give evidence for an increasing length scale for segmental dynamics, which would blow up at temperatures below T_g (see inset of Figure 1b). However, this cannot be directly demonstrated due to the lack of relaxation data for times longer than the laboratory scale.

The assumption of a temperature-dependent length scale is in line with the approach followed by Zetsche and Fischer[17] and later developed by Kumar and co-workers.[18] However, it worth remarking that the main differences with those previous approaches are (i) the explicit use of the AG model and (ii) the introduction of the essential ingredient of the self-concentration.

Acknowledgment. The authors acknowledge the University of the Basque Country and Basque Country Government (9/UPV 00206.215-13568/2001) and Spanish Minister of Education (MAT 2004-01617) for their support. The support of the European Community with the SoftComp program is also acknowledged.

References and Notes

(1) Colby, R. H. *Polymer* **1989**, *30*, 1275−1278.
(2) Alegría, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486−4492.
(3) Chung, G. C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 964−973.
(4) Lodge, T. P.; McLeish, T. C. B. *Macromolecules* **2000**, *33*, 5278−5284.
(5) He, Y.; Lutz, T. R.; Ediger, M. D. *J. Chem. Phys.* **2003**, *119*, 9956−9965.
(6) Kant, R.; Kumar, S. K.; Colby, R. H. *Macromolecules* **2003**, *36*, 10087−10094.
(7) Cangialosi, D.; Schwartz, G. A.; Alegría, A.; Colmenero, J. *J. Chem. Phys.* **2005**, *123*, 144908.
(8) Krygier, E.; Lin, G.; Mendes, J.; Mukandela, G.; Azar, D.; Jones, A. A.; Pathak, J. A.; Colby, R. H.; Kumar, S. K.; Floudas, G.; Krishnamoorti, R.; Faust, R. *Macromolecules* **2005**, *38*, 7721−7729.
(9) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139−146.
(10) Wolak, J. E.; Jia, X.; White, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 13660−13661.
(11) Wolak, J.; Jia, X.; Gracz, H.; Stejskal, E. O.; White, J. L.; Wachowicz, M.; Jurga, S. *Macromolecules* **2003**, *36*, 4844−4850.
(12) Wünderlich, B. ATHAS database, http://web.utk.edu/∼athas/.
(13) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Polym. Phys.* **1999**, *37*, 1023−1033.
(14) Leroy, E.; Alegría, A.; Colmenero, J. *Macromolecules* **2002**, *35*, 5587−5590.
(15) Cangialosi, D.; Alegría, A.; Colmenero, J. *Europhys. Lett.* **2005**, *70*, 614−620.
(16) Pérez, R.; Arbe, A.; Colmenero, J.; Frick, B.; Willner, L.; Richter, D.; Fetters, L. J. *Macromolecules*, submitted for publication.
(17) Zetsche, A.; Fischer, H. W. *Acta Polym.* **1994**, *45*, 168−175.
(18) Kamath, S.; Colby, R. H.; Kumar, S. K.; Karatasos, K.; Floudas, G.; Fytas, G.; Roovers, J. E. L. *J. Chem. Phys.* **1999**, *111*, 6121−6128.

MA052197R