상용성 고분자 혼합물의 미세 유변학

정 근창, B. H. Arendt*, J. A. Kornfield*

Microrheology of Miscible Polymer Blends

G.-C. Chung, B. H. Arendt*, and J. A. Kornfield*,
Lucky Research Park, Polymer Research Institute, Taejon.
*Chemical Engineering, California Institute of Technology
Pasadena, California 91125, U. S. A.

I. INTRODUCTION

Miscible blends exhibit viscoelastic behaviors that suggest that the individual species retain distinct motional characteristics, while their mobilities are sensitive to the composition of neighboring chains. The most pronounced examples are an anomalously broad glass transition [1] and failure of time-temperature superposition [2]. Related to the origin of these phenomena, dynamic heterogeneities have been studied recently both at a segmental [3] and a macromolecular level [4]. However, the effect of intrinsic dynamic differences between each species and that of compositional heterogeneity have not been resolved clearly, due to the lack of quantitative information on the dynamics of each species in the blend. Two-dimensional deuteron NMR (2D ^{2}H NMR) is used to quantitatively characterize the temperature and compositional dependence of the dynamics of each species. This method is sensitive to local segmental motions that have been associated with the glass transition. To determine the relationship between segmental motions and larger length scale relaxations that control melt rheology, we coordinate this study with a rheo-optical experiment on the contribution of each species to blend properties.

II. EXPERIMENTAL SECTION

Blends of polyvinylethylene (PVE) and polyisoprene (PI) are used as model systems, since they have been shown to be miscible in all proportions, yet have very weak interactions [5]. The synthesis and characterization results are reported elsewhere [6]. For ^{2}H NMR measurements, we use labeled blends, dPI/PVE and PI/dPVE, where dPI and dPVE denote deutero PI and PVE respectively. Blends are prepared and characterized as described previously [7]. The glass transition of the blends and pure components are characterized by differential scanning calorimetry (DSC) (Figure 1).

III. RESULTS AND DISCUSSION

The experimental 2D ^{2}H NMR spectra exhibit characteristic features of isotropic reorientation motion. Furthermore, a simple log-Gaussian distribution of correlation times provides a good description of the observed spectra. We determined from the experimental spectra two quantities that characterize the distribution of correlation times: the mean, $\langle \tau \rangle$, and the width, σ, of the distribution. The σ is much larger for each species in the blend than for homopolymers, particularly in 25/75 and 50/50 PI/PVE where broad glass transition is observed. The broad σ often gives rise to unwanted loss of NMR intensity associated with segmental motions in the range of correlation time, 10^{-6} s $\leq \tau \geq 10^{-4}$ s. The correction procedure is described elsewhere [7].

The corrected mean correlation times, τ_c, are plotted as a function of temperature and composition (Figure 3). The relaxation times determined from rheo-optical results are normalized as reported previously [7, 8] and are included for direct comparison (Figure 3, open symbols). The dotted lines are WLF fits with the fit parameters listed in Table I. The effective glass transition temperature, T_g^*, is defined as the temperature at which the τ_c reaches 1 s and is in good agreement with the DSC T_g for the two homopolymers (Figure 2). The C_1^g is fixed for each species, since we expect the extrapolated mobility at infinite temperature to be controlled by intrachain dynamic constraints, independent of composition.

The reported difficulty of using a single macroscopic T_g of blends as a reference temperature can be understood by considering the relative values of T_g^* for each species and the DSC T_g of the blend as a whole. The two T_g^*'s show different compositional dependence from each other and from the macroscopic DSC T_g (Figure 2). This implies that the compositional dependence of the component dynamics cannot be compensated simply by shifting the measurement temperature with respect to the blend T_g [4].

The failure of time-temperature superposition in PI/PVE blends can be described in terms of the different temperature dependence of the component dynamics. Though the dominant feature is the distinct individual T_g^*, the other parameter, C_2^g, also differs significantly and has a modest compositional dependence, in spite of the similarity between this parameter for the two pure species (Table I). In order to understand the compositional dependence of the WLF parameters, a free volume model is extended to a homogeneous blend. Fujita's free volume model postulates that the mobility of a particle in a condensed medium is governed by fractional free volume, $m = A \exp(-B/f)$, where m is the mobility, A is the intrinsic mobility at infinite free volume, B is a structural parameter for a given molecule and f is the fractional free volume. Under the hypothesis that

both species share the same fractional free volume in a homogeneous blend, we obtain WLF equations for individual species in a homogeneous blend, $\log(\tau_{c,i}) = \log(A_i) + \frac{B_i}{\alpha(\phi)[T-T_0(\phi)]}$, where α is the thermal expansion coefficient of free volume, ϕ is the mole fraction of species i, $C_{1,i}^g = -\log(A_i)$ and $C_{2,i}^g * C_{1,i}^g = B_i/\alpha(\phi)$. The intrachain dynamic constraints for individual species represented as A_i and B_i are independent of blend ratio, while $\alpha(\phi)$ and $T_0(\phi)$ are properties of blend as a whole. Considering the uncertainties introduced in the WLF analysis, the free volume model appears to be consistent with the WLF fit: T_0 appear to be reasonably close for both species in the blend, and the ratio of $C_2^g * C_1^g$ between PI and PVE, R, is nearly constant for three compositions studied here. In fact, a reasonable WLF fit can be obtained under the constraint that T_0 for both species are identical at a given composition, for which the ratio of $C_2^g * C_1^g$ has similar value. Therefore, in light of the free volume model, we can expect a pronounced thermorheological complexity when the A_i and B_i for the two homopolymers are significantly different. In real blend, however, the actual temperature dependence of rheological properties can be considerably more complicated due to additional effects of compositional heterogeneity.

REFERENCES

1. Lau, S.; Pathak, J.; Wunderlich, B. *Macromolecules*, **15**, 1278 (1982).
2. Roovers, J.; Toporowski, P. M. *Macromolecules*, **25**, 3454 (1992).
3. Roland, C. M.; Ngai, K. L. *Macromolecules*, **24**, 2261 (1991).
4. a) Zawada, J. A.; Ylitalo, C. M.; Fuller, G. G.; Colby, R. H.; Long, T. E. *Macromolecules*, **25**, 2896 (1992). b) Composto, R. J.; Kramer, E. J.; White, D. M. *Polymer*, **31**, 2320 (1990).
5. a) Heffner, S. A.; Mirau, P. A. *Macromolecules*, **27**, 7283 (1994). b) Tomlin, D. W.; Roland, C. M. *Macromolecules*, **25**, 2994 (1992).
6. Chung, G.-C.; Kornfield, J. A.; Smith, S. D. *Macromolecules*, **27**, 964 (1994).
7. Chung, G.-C.; Kornfield, J. A.; Smith, S. D. *Macromolecules*, **27**, 5729 (1994).
8. Arendt, B. A.; Kannan, R. M.; Zewail, M.; Kornfield, J.A.; Smith, S. D. *Rheol. Acta* **33**, 322 (1994).

Table I. The best fit WLF parameters

dPI/PVE	C_1^g	C_2^g	T_g^*	T_0	PI/dPVE	C_1^g	C_2^g	T_g^*	T_0	R
100/0	12.9	50	211	161						
75/25	12.9	50	217	167	75/25	12.3	68	225	157	0.77
50/50	12.9	47	226	179	50/50	12.3	65	234	169	0.76
25/75	12.9	45	237	192	25/75	12.3	58	253	195	0.81
					0/100	12.3	49	271	223	

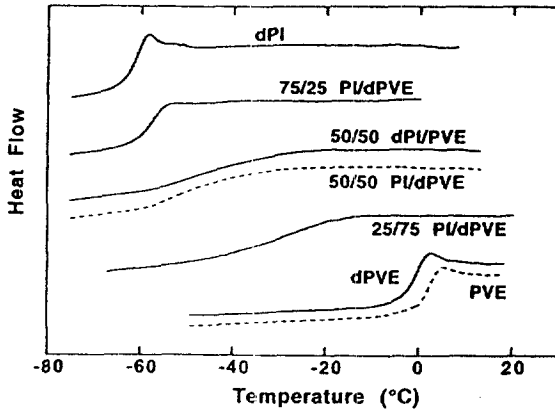**Figure 1.** DSC traces for the homopolymers and the blends.

Figure 2. Compositional dependence of T_f^*'s and T_g of the blends. The upper and lower bounds of T_g are indicated by $-$ symbol. The differences between the T_g^* and the DSC T_g are also displayed (inset).
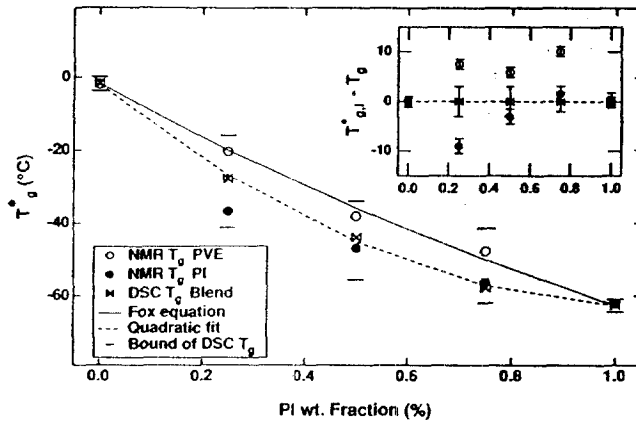

Figure 3. The comparison of NMR (solid symbols) and rheo-optical (open symbols) results.