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Closed-Loop Miscibility Gaps in Polymer Blends under Shear Flow

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To model the effects of shear flow on polymer blends, we recently[1,2] proposed a model which included finite stress relaxation times for each of the components in a modified equation of motion for concentration fluctuations. We showed that the conditions for the growth of small concentration fluctuations are altered from that of the quiescent blend. While the results reported in refs 1 and 2 explain many of the unusual phenomena, such as shifts in the phase boundary, we were unable to account for closed-loop miscibility gaps, which have been reported.[3,4] Such gaps were inferred from the growth of concentration fluctuations, in the vorticity (z) direction, below the quiescent spinodal temperature, in a blend of solution-chlorinated polyethylene (SCPE) and poly(ethylene-co-vinyl acetate) (EVA), subjected to shear flow.

In our model the blend is treated as two chemically dissimilar, monodisperse components, A and B, with respective volume fractions, ϕ_A and ϕ_B, such that $\phi_A + \phi_B = 1$. In ref 1 we showed that the linearized equation of motion for a concentration fluctuation $\delta\phi_A(q,t)$, of component A, under the influence of shear in the q_z direction, can be written as

$$\frac{\partial \delta\phi_A(q_z,t)}{\partial t} = -{q_z}^2 D_{\text{eff}} \delta\phi_A(q_z,t) \qquad (1)$$

where D_{eff} is the effective diffusion coefficient. Near the phase boundary of a polymer blend the relaxation time of concentration fluctuations becomes very large and is much greater than the stress relaxation time. At the phase boundary the divergent concentration fluctuation relaxation time results in the condition $D_{\text{eff}} = 0$ for $q \to 0$. If $D_{\text{eff}} < 0$, first-order fluctuations become unstable and grow, rather than relax. As will be shown, D_{eff} depends on the quiescent thermodynamics of the blend and the normal force arising from the network stress. In ref 1 we modeled the latter using the double-reptation concept.[5−7] Physically, double reptation accounts, in a simple way, for the fact that polymers do not reptate in fixed tubes, as assumed in the original tube model.[8] Hence, in polymer blends stress relaxation depends not only on the dynamics of each individual polymer but also on the dynamics of the surrounding polymers. At low enough shear rates an adequate description of the relation between stress and shear rate in polymer blends is provided by the Maxwell model[9] combined with the double-reptation model. If we assume that stress relaxation can be described as a single-exponential process,[8] in the steady state the normal force component of the steady-state network stress in the vorticity direction, σ^n_{zz}, is given by

$$\sigma^n_{zz} = -\frac{2}{3}\dot{\gamma}^2\left[{\phi_A}^2 G_A {\tau_A}^2 + 8\phi_A(1-\phi_A)(G_A G_B)^{1/2}\left(\frac{\tau_A\tau_B}{\tau_A+\tau_B}\right)^2 + {\phi_B}^2 G_B {\tau_B}^2\right] \qquad (2)$$

where $\dot{\gamma}$ is the shear rate, τ_i is related to the relaxation time of each component in a fixed network of obstacles with a composition identical to that of the blend,[10] and G_i is the plateau modulus per monomer volume of component i, given by[8] $G_i/k_BT \simeq 1/N_{ie}$.

As discussed in refs 11, 12, and 1, there is no perturbation of the shear rate in the vorticity direction; i.e., $\dot{\gamma}(z)$ is constant. Hence, combining eqs 1 and 2 we have[1]

$$D_{\text{eff}}(q_z) = 2M[\chi_c - \chi + \kappa {q_z}^2 + \Delta\chi_c(q_z)] \qquad (3)$$

where κ is the interfacial tension, χ is the Flory−Huggins interaction parameter, and χ_c is its value on the quiescent spinodal. In eq 3,

$$\Delta\chi_c(q_z) = \frac{2\alpha}{3k_BT}\dot{\gamma}^2 G_A {\tau_A}^2\left\{\phi_A + 4(1-2\phi_A)G'^{1/2}\left(\frac{\tau'}{1+\tau'}\right)^2 - (1-\phi_A)G'\tau'\right\} \qquad (4)$$

where $G' = G_B/G_A$ and $\tau' = \tau_B/\tau_A$.The effect of shear is proportional to the term[13]

$$\alpha = \frac{(N_A/N_{Ae}){\zeta_0}^A - (N_B/N_{Be}){\zeta_0}^B}{(N_A/N_{Ae})\phi_A{\zeta_0}^A + (N_B/N_{Be})(1-\phi_A){\zeta_0}^B} \qquad (5)$$

where N_i is the degree of polymerization of an entire chain, N_{ie} is the degree of polymerization of an entanglement segment, and ${\zeta_0}^i$ is the monomeric friction coefficient, of component i. As discussed in some detail in refs 1 and 2, $\Delta\chi_c(q_z)$ can be positive or negative, depending on the values of G' and τ'.

In ref 1 we assumed the various rheological parameters to be equal at all temperatures. Although many of the characteristics of the blend vary with temperature, we believe that the most significant factor is the temperature dependence of the monomeric friction coefficient, ${\zeta_0}^i$. In pure melts, ζ_0 changes rapidly with temperature, and a suitable description of the behavior is provided by the phenomenological Williams−Landel−Ferry (WLF) formula[14]

$$\log \zeta_0(T) = \log \zeta_0(\mathrm{T}_0) + \frac{-c_1^0(T-T_0)}{c_2^0 + T - T_0} \qquad (6)$$

where T_0 is a reference temperature, which is often chosen to be the glass-transition temperature,[15] and c_1^0 and c_2^0, are empirical constants.

The situation in blends of different polymers is much less well-understood, despite the attention that has recently been devoted to the subject.[16−19] It is

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generally observed that blends in the miscible state are thermorheologically complex; i.e., it is not possible to determine a single set of WLF parameters that will lead to time−temperature superposition at all frequencies. Colby[16] has suggested that a reasonable description of the monomeric friction coefficient for each component in the blend can be obtained by using c_1^0 and c_2^0 as measured for the pure components and T_g as measured for the blend. Consequently, the local dynamics of the two components are coupled through the use of a single T_g. However, each component friction factor has its own distinct temperature dependence, which is in agreement with observations.[16,20,21] More sophisticated theoretical schemes have been suggested,[22,23] which propose that local concentration fluctuations result in a range of local dynamic environments. Such an idea is successful in describing the broad range of glass-transition temperatures that are observed in polymer blends. However, these models remain phenomenological, in that it is still assumed that each component retains its own WLF parameters upon blending.[23] In this note, we use the original idea proposed by Colby[16] since it captures the underlying physical behavior in a manner ideal for our analysis.

The important consequence of applying eq 6, using pure component values for c_1^0 and c_2^0, and the blend T_g, is that the ratio of the monomeric friction coefficients is temperature-dependent. This in turn leads to temperature dependence of both α (see eq 5) and τ'. In the tube model the relaxation time of each component is given by[8] $\tau_i = \zeta_0{}^i N_i{}^3 b_i{}^2/\pi^2 k_B T N_{ei}$. Hence, if we assume the statistical segment lengths of each component to be equal, we can see that the response of the blend to shear flow is characterized by three independent parameters for each component, the degree of polymerization of an entanglement segment, N_{ie}, the degree of polymerization of a chain, N_i, and the monomeric friction coefficient, $\zeta_0{}^i$. Equivalently, we may use N_i, N_{ie}, and the terminal relaxation time τ_i, fixed at some arbitrary temperature, as our independent parameters. The temperature dependence of τ_i is then governed by the WLF equation, with the appropriate parameters.

We illustrate the possible consequences of such behavior for a model system, based on the SCPE/EVA blend studied in ref 4. This blend phase separates upon heating; that is, it exhibits a lower critical solution temperature. We have estimated the following relationship between χ and temperature, $\chi = 0.011 - (3.8/T)$, using experimentally determined spinodal temperatures for two different 50/50 SCPE/EVA blends.[24] The quiescent spinodal curve is found from the Flory−Huggins free energy.[25] We also include a concentration dependence of the glass-transition temperature, by use of the Fox−Flory relation[14]

$$\frac{1}{T_g} = \frac{\phi_A}{T_{gA}} + \frac{\phi_B}{T_{gB}} \tag{7}$$

where T_g is the glass-transition temperature of the blend and T_{gi} is the glass-transition temperature of pure component i.

The outcome of eq 3 for the phase behavior is illustrated in Figure 1, with the relevant model parameters given in Table 1. For the stated WLF parameters τ' increases with temperature. For each curve, $\dot{\gamma}$ is constant for all temperatures and compositions, and the relaxation times of each component are fixed (arbitrarily) at $T = 355$ K. From eq 3, it can be seen that the effect of shear is proportional to $(\dot{\gamma}\tau_A)^2$, and since τ_A decreases rapidly with temperature, the effect of shear is less noticeable at higher temperatures. This is illustrated by the smaller shifts in the phase boundary which occur at higher temperatures. The results clearly illustrate that, for a small range of shear rates, it is possible to induce miscibility gaps, if the relative relaxation time, τ', and the relative plateau modulus, G', satisfy certain criteria. A necessary, but not sufficient, condition being that if $G' > 1$, then $\tau' < 1$. In Figure 2 we illustrate the typical behavior of the effective diffusion coefficient, D_{eff}, as a function of temperature for $\phi_A = 0.3$ and $\dot{\gamma} = 5.5$. A significant difference between our results and the experimental observations is the temperature range over which closed-loop miscibility gaps occur. Experimentally,[4] the range is only 10° below the quiescent spinodal; our model suggests a typical range of 20−30°. This difference may be due to a lack of accurate rheological data.

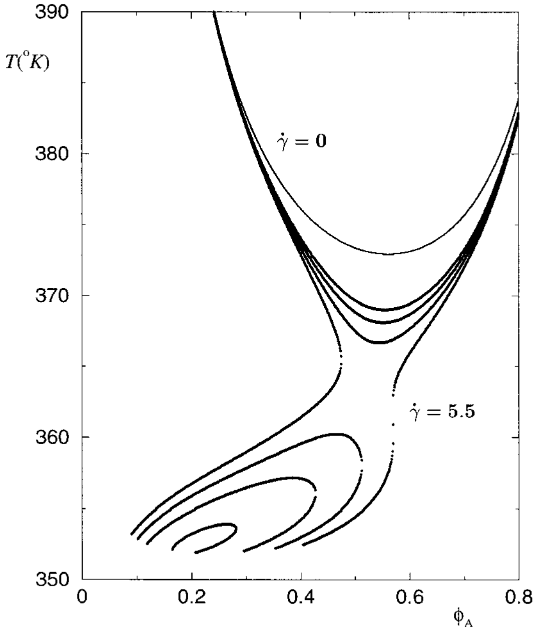

Figure 1. Effect of shear on first-order fluctuations, as determined from eq 3, for a blend with parameters given in Table 1. The three unlabeled curves are $\dot{\gamma} = 4.75$ (for the innermost miscibility gap and the shifted spinodal closest to the $\dot{\gamma} = 0$ curve), $\dot{\gamma} = 5.0$, and $\dot{\gamma} = 5.25$. The behavior for shear rates of $\dot{\gamma}\tau_A > 0.75$ was not calculated since at such reduced shear rates the weakly Newtonian theory we have used is not applicable.

Table 1. Parameters Used for the Model Calculation[a]

component	m_0	N	N_e	$\tau(T = 355\text{ K})$	c_1	c_2	T_g
A	54	1960	75	0.1	16.0	60.0	248.0
B	103	3300	15	0.05	12.0	60.0	306.0

[a] m_0 are the monomer molecular weights for (A) EVA and (B) SCPE. N_e for component A is an average of the behavior of polyethylene and polyvinyl acetate, while N_e for component B was chosen to be representative of the behavior of polyethylene.[27] The WLF parameters are based on values expected for polyvinyl acetate (component B) and polyethylene (component A).[15] The glass-transition temperatures for each component were measured in ref 4.

Finally, we note that while we have accounted for a concentration dependence of the glass-transition temperature, we have not included the additional contributions to the gradient of the stress which arise from gradients in the monomeric friction factor. Once we have

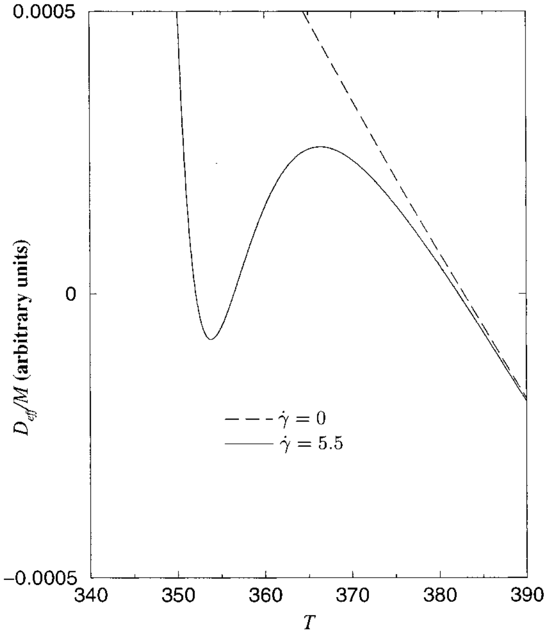

Figure 2. An example of the effective diffusion coefficient, $D_{\rm eff}$, as defined in eq 3, for the parameters given in Table 1, with $\phi_{\rm A} = 0.3$. For comparison the zero shear limit is included. If $D_{\rm eff} < 0$, then small concentration fluctuations grow. The contours of Figure 1 are determined from the condition $D_{\rm eff} = 0$.

determined the temperature dependence of the relaxation times using the appropriate blend T_g, we assume the relaxation times to be fixed and not a function of concentration. Hence, our theory is strictly only applicable to blends in which each component has a similar glass-transition temperature. Despite attempts to understand and explain the consequences that such behavior will have on blend rheology, a clear picture has yet to emerge.[22,23] Another possible factor that we have neglected is the effect of shear flow on the glass-transition temperature. Since the phase boundaries are well above the glass-tranisition temperature, we may expect that this does not play too important a role.

In summary, our results indicate that closed-loop miscibility gaps are probably an exception, requiring a delicate balance of the governing parameters. In most blends, shear will simply shift the spinodal. The delicacy of the criteria necessary to explain closed-loop miscibility gaps may go some way to explaining why only a few experimental systems have been found to display them.[26] In relaxing the constraint of the ratio of the relaxation time being temperature-independent, we believe that the theory represents an important step in developing a physical picture that accounts for the important underlying mechanisms driving the response of polymer blends to shear flow.

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