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Shear flow effects on phase separation of entangled polymer blends

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We introduce an entanglement model mixing rule for stress relaxation in a polymer blend to a modified Cahn-Hilliard equation of motion for concentration fluctuations in the presence of shear flow. Such an approach predicts both shear-induced mixing and demixing, depending on the relative relaxation times and plateau moduli of the two components. [S1063-651X(98)51404-3]

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Although the effects of shear flow on polymeric systems have been studied experimentally [1,2] and theoretically, a consistent overall picture has yet to emerge. It is believed that hydrodynamic effects in simple binary liquids [3] lead to shear-induced mixing, whereas viscoelasticity in polymer solutions may lead to shear-induced phase separation [4,5]. Doi and Onuki [6] established a useful theoretical framework from which to study entangled polymer blends under shear flow. However, they did not explore the important difference between a solution and a blend. In an entangled polymer solution it is reasonable to assume that all of the stress is carried by the polymer chain, and that, for well entangled polymers [7], the stress relaxes with a single characteristic time τ. In an entangled blend each component has its own characteristic relaxation time and plateau modulus. Reference [6] included only a single relaxation time.

A number of unusual effects on polymer blend miscibility, not observed in polymer solutions, such as flow-induced demixing at low shear rates, but demixing at higher shear rates, were reported in Ref. [1]. It was also noted that the greater the difference in viscosity between the blend components, the larger the effect of shear on the miscibility of the system. Finally, there was evidence of miscibility gaps at temperatures lower than the quiescent spinodal curve. An understanding of such phenomena is the motivation behind this work.

Physically, we may anticipate that unusual behavior in shear flow should be associated uniquely with polymer blends. It is known that, in a blend of long and short polymers, long polymers relax more quickly in the presence of short polymers than in a monodisperse melt, and that short polymers also relax more quickly in the presence of other short polymers than in a blend. This has been modeled in polydisperse homogeneous blends by ‘‘double reptation’’ [8], as described below. In this Rapid Communication, we show that, for heterogeneous blends, coupled effects in stress relaxation result in an effective dynamic competition between the components, both of which prefer to be in the presence of short polymers in order to reduce stress in the presence of shear flow.

The two key assumptions of Ref. [6] are that there exists a ‘‘tube velocity,’’ which arises from the difference in diffusion coefficients between the two components (an idea originally introduced by Brochard [9]), and that the stress arising from the shear flow enters the dynamic equations at the same level as the chemical potential. In other words, stress gradients become an extra driving force for the dynamics of concentration fluctuations. The force balance equations for the two components are written as [6]

$$\zeta(\vec{v}_A-\vec{v}_B)+\phi_A\vec{\nabla}\mu_A+\phi_A\vec{\nabla}p-\frac{\zeta_A}{\zeta_A+\zeta_B}\,\nabla\cdot\underline{\underline{\sigma}}^{(n)}=\vec{0},$$
$$\zeta(\vec{v}_B-\vec{v}_A)+\phi_B\vec{\nabla}\mu_B+\phi_B\vec{\nabla}p-\frac{\zeta_B}{\zeta_A+\zeta_B}\,\vec{\nabla}\cdot\underline{\underline{\sigma}}^{(n)}=\vec{0},\tag{1}$$

where $\vec{v}_i$ is the velocity of component i; $\zeta_i=\phi_i(N_i/N_{ei})\zeta_0$ is the corresponding frictional drag, where N_i and N_{ei} are the degree of polymerization of a chain and an entanglement segment, respectively; ϕ_i is its volume fraction; ζ_0 is the monomeric friction coefficient, which for simplicity we shall assume to be equal for both species; $\zeta=\zeta_A\zeta_B/(\zeta_A+\zeta_B)$. The first term of Eq. (1) represents the drag force between the two components. μ_i is the chemical potential, so that the second term represents the force due to the osmotic pressure; p is the isotropic pressure that ensures incompressibility; and $\sigma^{(n)}$ is the network stress due to the shear flow effects. If we eliminate the pressure from Eq. (1), then

$$\zeta(\vec{v}_A-\vec{v}_B)=\phi_A\phi_B[-\vec{\nabla}(\mu_A-\mu_B)+\alpha\vec{\nabla}\cdot\underline{\underline{\sigma}}^{(n)}],\tag{2}$$

where

$$\alpha=[(\zeta_A/\phi_A)-(\zeta_B/\phi_B)]/(\zeta_A+\zeta_B).$$

By inserting Eq. (2) into the continuity equation

$$\partial\phi_A/\partial t=-\vec{\nabla}\cdot(\vec{v}_A\phi_A),$$

the key result of Ref. [6] is obtained:

$$\frac{\partial\phi_A}{\partial t}=-\vec{\nabla}\cdot(\vec{v}\phi_A)+\vec{\nabla}(\phi_A^2\phi_B^2/\zeta)[\vec{\nabla}(\mu_A-\mu_B)-\alpha\vec{\nabla}\cdot\underline{\underline{\sigma}}^{(n)}],\tag{3}$$

where $\vec{v}=\phi_A\vec{v}_A+\phi_B\vec{v}_B$ is the volume average velocity.

It is now obvious that before proceeding, we must consider the form that the network stress should take. For a polymer solution or melt, the network stress is minimally modeled by the Maxwell model [10]

$$\underline{\underline{\sigma}}^{(n)}(t)=\int_{-\infty}^{t}\frac{\partial G(t-t')}{\partial t'}\,\underline{\underline{C}}^{-1}(t,t')dt',\tag{4}$$

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where $\underline{\underline{\sigma}}^{(n)}$ is only determined to within an isotropic constant, $G(t-t')$ is the stress relaxation function, and $\underline{\underline{C}}^{-1}$ is the Finger tensor, which for simple shear flow takes the form

$$\underline{\underline{C}}^{-1}(t,t')=\begin{pmatrix} 1+\dot{\gamma}^2(t-t')^2 & \dot{\gamma}(t-t') & 0 \\ \dot{\gamma}(t-t') & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (5)$$

In Eq. (5), and for the remainder of this Rapid Communication, we use the usual directional conventions for flow (x), shear gradient (y), and vorticity (z). In order to elucidate the features of shear flow, which are of the greatest interest when considering the coupling of stress to concentration fluctuations, we assume that for a single polymeric component, it is sufficient to consider the stress relaxation as dominated by a single time scale τ, so that,

$$G(t-t')=G_0\exp\{-(t-t')/\tau\},$$

where G_0 is the plateau modulus. In the steady state, Eq. (4) gives rise to the following expressions for the shear stress and first normal stress difference:

$$\sigma_{xy}=G_0\dot{\gamma}\tau, \quad N_1=\sigma_{xx}-\sigma_{yy}=G_0(\dot{\gamma}\tau)^2. \qquad (6)$$

For polymer blends it is essential to understand how the rheological behavior of a mixture is related to the component rheology. It is well established [11,12] that a simple linear mixing rule, which results from the reptation model in its original form [7], is inappropriate for describing the rheological behavior of polydisperse systems. A more realistic mixing rule, known as double reptation [8], was derived by extending the reptation concept to allow for the simultaneous relaxation of network constraints on a given chain by reptation of its neighbors. This is the simplest way to treat constraint release in polymer blends [13]. By generalizing double reptation to blends, and again assuming single exponential stress relaxation for each component, we have

$$G(t-t')=(\phi_A\{G_A\exp[-(t-t')/\tau_A]\}^{1/2} + \phi_B\{G_B\exp[-(t-t')/\tau_B]\}^{1/2})^2. \qquad (7)$$

Such a mixing rule is highly successful in predicting stress relaxation in polymer blends [14]. The key features captured by this theory are that the relaxation behavior of the two components is coupled, with the degree of coupling being dependent on the relative concentrations of the two components, and that the dependence of the various stresses on the component volume fractions is given explicitly. We expect the validity of Eq. (7) to extend into the weakly nonlinear flow regime where N_1 is important, because the stress relaxation is still controlled by reptation, rather than by nonlinear processes such as retraction [7], for which cooperative motion becomes more subtle [15]. Use of Eq. (7) gives the steady-state stresses as

$$\sigma_{xy}=\dot{\gamma}\left[\phi_A^2G_A\tau_A+4\phi_A\phi_B(G_AG_B)^{1/2}\left(\frac{\tau_A\tau_B}{\tau_A+\tau_B}\right)+\phi_B^2G_B\tau_B\right],$$

$$N_1=\sigma_{xx}-\sigma_{yy}=2\dot{\gamma}^2\left[\phi_A^2G_A\tau_A^2+8\phi_A\phi_B(G_AG_B)^{1/2} \times\left(\frac{\tau_A\tau_B}{\tau_A+\tau_B}\right)^2+\phi_B^2G_B\tau_B^2\right]. \qquad (8)$$

Since we can only determine the stress to within an isotropic constant, we may rewrite the diagonal components of the stress tensor in terms of the first normal force,

$$\sigma_{xx}=2N_1/3, \quad \sigma_{yy}=-N_1/3, \quad \sigma_{zz}=-N_1/3,$$

so that $\mathrm{Tr}\underline{\underline{\sigma}}=0$.

Now we Fourier transform and linearize Eq. (3), using the adiabatic approximation [5], in which it is assumed that the stress relaxes instantaneously to a value consistent with the magnitude of the concentration fluctuation; in other words, we neglect the equation of motion for the stress. This is a good approximation for most experimental systems [1,2], which possess such a separation of time scales. It should be noted that, while we have assumed small concentration fluctuations and, hence, small stress fluctuations, we have not placed any restriction on the magnitude of the stress. The result is

$$\frac{\partial\delta\phi_A}{\partial t}=-\dot{\gamma}q_x\frac{\partial\delta\phi_A}{\partial q_y}+M\left[q^2(\chi_c-\chi+\kappa q^2) -\frac{\alpha}{k_BT}\sum_{i,j}q_iq_j\frac{\partial}{\partial\phi_A}\sigma_{ij}^{(n)}\right]\delta\phi_A, \qquad (9)$$

where $M=\phi_A^2\phi_B^2k_BT/\zeta$ is the mobility. We have used the usual expression for the chemical-potential difference in terms of χ, the Flory-Huggins interaction parameter, χ_c, its value on the quiescent spinodal, and κ, the interfacial energy. We may define an effective diffusion coefficient D_{eff} by

$$\partial\delta\phi_A/\partial t=-D_{\mathrm{eff}}q^2\delta\phi_A. \qquad (10)$$

The addition of stress gradients to the driving force for the dynamics of concentration fluctuations leads to a modified diffusion coefficient. Since the phase boundary is given by $D_{\mathrm{eff}}\to 0$, in the limit of $q\to 0$, we have the possibility of shear-induced shifts in the phase boundary. However, concentration fluctuations in the q_x direction, even those that in quiescent conditions would grow after a jump into the two-phase region, will be convected to larger q and eventually decay. Consequently, shifts in the phase boundary can only be defined in the $q_x=0$ plane. If we consider the contribution to the stress gradient arising from the first normal stress difference, then significant effects on the static ‘‘equilibrium’’ properties arise. The main result of Eq. (9) for polymer solutions [4,5] is that shear-induces phase separation in the q_y direction and suppresses it in the q_z direction.

Here we focus on the consequences for polymer blends. First, we consider the q_y direction for which $q_x=q_z=0$. We need an expression for the variation of the velocity (or shear) field in the q_y direction. If we eliminate the relative velocities from Eq. (1), then

$$\phi_A\vec{\nabla}\mu_A+\phi_B\vec{\nabla}\mu_B+\vec{\nabla}p-\vec{\nabla}\cdot\underline{\underline{\sigma}}^{(n)}=\vec{0}, \tag{11}$$

from which we find

$$\vec{\nabla}\times\vec{\nabla}\underline{\underline{\sigma}}^{(n)}=\vec{0}, \tag{12}$$

the result of which is that the shear stress σ_{xy} is constant in the velocity gradient direction, and as a consequence [4],

$$\left.\frac{\partial\dot{\gamma}}{\partial\phi_A}\right|_{\sigma_{xy}}=-\left(\frac{\partial\sigma_{xy}}{\partial\phi_A}\right)_{\dot{\gamma}}\Big/\left(\frac{\partial\sigma_{xy}}{\partial\dot{\gamma}}\right)_{\phi_A}. \tag{13}$$

We now assume that the steady-state stress is given by Eq. (8). By substituting Eq. (13) into Eq. (9), and defining $G'=G_B/G_A$ and $\tau'=\tau_B/\tau_A$, we have

$$\begin{aligned}D(\vec{q}_y)&\equiv 2M[\chi_c-\chi+\kappa q_y^2+\Delta\chi_c(\vec{q}_y)],\\&=2M(\chi_c-\chi+\kappa q_y^2)+\frac{4}{3}M\frac{\alpha}{k_BT}\\&\times\dot{\gamma}^2G_A\tau_A^2\Bigg[\phi_A+4(1-2\phi_A)G'^{1/2}\left(\frac{\tau'}{1+\tau'}\right)^2\\&-(1-\phi_A)G'\tau'^2-2\{\phi_A{}^2+8\phi_A(1-\phi_A)\\&\times G'^{1/2}\left(\frac{\tau'}{1+\tau'}\right)^2+(1-\phi_A)^2G'\tau'^2\}\\&\times\left\{\frac{\phi_A+2(1-2\phi_A)G'^{1/2}\left(\frac{\tau'}{1+\tau'}\right)-(1-\phi_A)G'\tau'}{\phi_A^2+4\phi_A(1-\phi_A)G'^{1/2}\left(\frac{\tau'}{1+\tau'}\right)+(1-\phi_A)^2G'\tau'}\right\}\Bigg]\end{aligned} \tag{14}$$

which defines $\Delta\chi_c(\vec{q}_y)$, the $\dot{\gamma}$-dependent shift in the spinodal in the q_y direction. The convective term is absent due to the condition on q_x. Although the shift in the spinodal is given by a somewhat cumbersome term, there are some important general comments that can be made. It should be noted that when $N_A>N_B$ we have $\alpha>0$; to ensure positivity we assume, without loss of generality, that component A has the greater relaxation time, i.e., $\tau_A>\tau_B$.

An examination of Eq. (14) reveals that the shift in the spinodal ($\Delta\chi_c$) can be either positive or negative, depending on the relative values of G_A, G_B, τ_A, and τ_B. In other words, it is possible to suppress phase separation in the q_y direction by the mechanism of shear, a phenomenon that is not predicted for polymer solutions. In Fig. 1 we show the curve corresponding to zero shift in the spinodal for a range of G' and $\tau'<0$. The complex behavior for $G'<1$ is particularly remarkable. The range of ϕ_A for which phase separation is suppressed is reduced as G' decreases from unity, whereas, for $G'>1$, the corresponding range is increased as G' increases from unity. In the limit of $G'\rightarrow 0$, the predictions of Refs. [4,5] are recovered with a quadratic dependence of the shear modulus on concentration, and a relaxation time that is independent of concentration.

The difference between $q_x=q_y=0$ and the $q_x=q_z=0$ direction is that no shear rate perturbation is required [5] to satisfy Eq. (12); $\dot{\gamma}$ is constant. Hence, in the q_z direction, the shift in the spinodal is given by

$$\begin{aligned}\Delta\chi_c(\vec{q}_z)=\frac{2\alpha}{3k_BT}\dot{\gamma}^2G_A\tau_A^2\Bigg[\phi_A+4(1-2\phi_A)G'^{1/2}\left(\frac{\tau'}{1+\tau'}\right)^2\\-(1-\phi_A)G'\tau'\Bigg].\end{aligned} \tag{15}$$

In the case of $G'\leqslant 1$, we see from Eq. (15) that the spinodal in the q_z direction will always be suppressed, independently of τ', even though the spinodal in the q_y direction may be enhanced or suppressed. For $G'>1$ it is possible to induce phase separation for a range of τ'. This is illustrated in the inset of Fig. 1. For polymer solutions, i.e., $G'\rightarrow 0$, the spinodal becomes suppressed in this direction, as predicted by Milner [5].

The rich behavior described above is entirely due to the coupling of the stress relaxation of the two components. The underlying physics, which gives rise to Eqs. (14) and (15), is that each component can relax stress more effectively when surrounded by polymers with the faster relaxation time and/or the lower plateau modulus. This gives rise to an effective competition between the two components, the result of which depends sensitively upon the relative relaxation times and the relative plateau moduli. These factors, combined with the variation of the normal force with concentration and the constraints imposed by the force balance [Eqs. (11) and (12)], all determine whether the shift in the phase boundary is positive or negative.

It is well established that polymers exhibit shear thinning flow behavior at relatively small shear rates, due to the long relaxation times of many polymers, and we expect shear thinning to have a strong effect on the demixing behavior. In order to extend the above work to this regime of strong flow, a constitutive equation is required. Doi and Edwards were

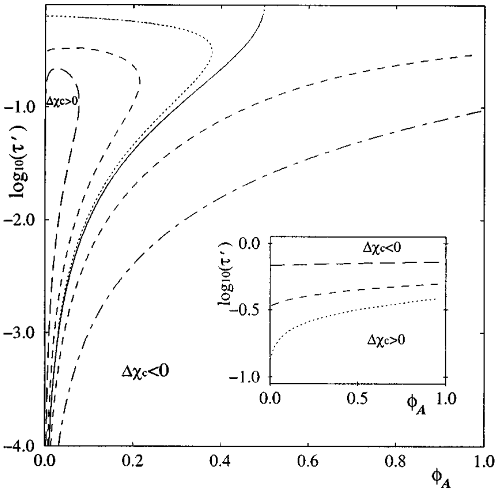

FIG. 1. Contour plots of zero shift in the spinodal for fluctuations in the q_y direction for a range of G' as a function of τ' and ϕ_A. In the region to the right of each curve, shear-induced demixing ($\Delta\chi_c<0$) occurs, and to the left, shear-induced mixing ($\Delta\chi_c>0$) occurs. −−−, $G'=0.1$; ---, $G'=0.5$; ··· $G'=0.9$; ——, $G'=1.0$; ---, $G'=2.0$; -·-, $G'=10.0$. Inset: same as main figure, but for fluctuations in the q_z direction. In the region above each curve, shear-induced demixing ($\Delta\chi_c<0$) occurs, and below, shear-induced mixing ($\Delta\chi_c>0$) occurs. −−−, $G'=2.0$; ---, $G'=5.0$; ..., $G'=10.0$.

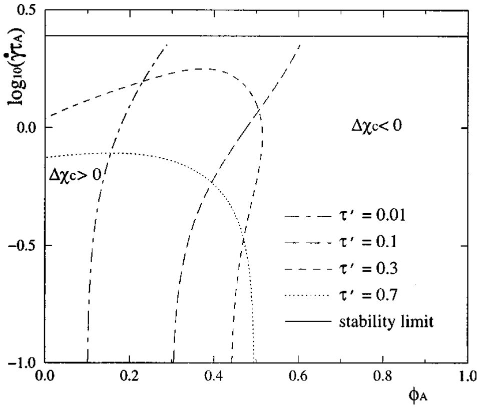

FIG. 2. A map of the regions of shear-induced mixing ($\Delta\chi_c > 0$) and shear-induced demixing ($\Delta\chi_c < 0$) as a function of shear rate, in the q_y direction, for a range of τ'. In all cases, $G' = 1.0$. The diagram illustrates the change in the miscibility behavior as shear thinning becomes important for $\log_{10}(\dot{\gamma}\tau_A) < -0.5$. For values of $\dot{\gamma}\tau_A$ greater than the stability limit, the constitutive equation produces physically unrealistic solutions.

the first to derive such an equation based on the tube model [7]. The physical picture of their model is that after deformation a polymer retracts quickly, *within* its tube, to its equilibrium length, followed by slow orientational relaxation. Such behavior leads to the prediction of shear thinning, with a shear viscosity and first normal stress, which both decrease for $\dot{\gamma}\tau \geqslant 1$. An important feature of the model is that the stress relaxation function is identical to that used before; hence, the strain-dependent nonlinearities can be factored, in agreement with experiments on polymer melts and solutions [7]. Consequently, we can apply [18] the mixing rule of des Cloiseaux to the shear thinning regime. Again, there is no dependence of the relaxation times and plateau moduli on the volume fraction within this approximation. Before proceeding, it is important to note that a significant problem, which is the subject of considerable ongoing research [15,16] with this model, is that, above a critical shear rate, the shear stress decreases with shear rate, which is physically unrealistic. Hence, we shall restrict our attention to the values of $\dot{\gamma}\tau$ for which $\partial\sigma_{xy}/\partial\dot{\gamma} > 0$. This regime is nonetheless interesting, since shear thinning still occurs.

By using a differential approximation [17] to the Doi-Edwards model, we find that the behavior of the shift in the spinodal, in the q_y direction, is altered from that of weakly nonlinear flow. In Fig. 2 we illustrate the regions of positive and negative shifts in the spinodal in the q_y direction; as $\dot{\gamma}$ is increased and shear thinning becomes important, the miscibility behavior changes. Without shear thinning the effect of increasing the shear rate is to increase the magnitude of the shift in the phase boundary; however, if shear thinning effects are included, the sign of the shift can also change. For $\tau' = 0.01$ and $\tau' = 0.1$, the behavior, for a range of ϕ_A, changes from shear-induced demixing to shear-induced mixing. Such qualitative behavior has been seen in experiments in polystyrene-polyvinylmethylether blends [2]. However, for $\tau' = 0.3$ and $\tau' = 0.7$, shear-induced demixing becomes favorable as shear thinning of both components occurs. Such complex behavior arises from the variation of the normal force with the relative concentration of each component; the underlying physical reasons will be explored further in Ref. [18].

In summary, we have shown that a simple mixing rule for stress relaxation, coupled with a phenomenological equation of motion for concentration fluctuations in the presence of shear flow, leads to rich, but quantifiable, changes in the phase diagrams of polymer blends, which are qualitatively different from that of polymer solutions. Our results may help to explain some of the phenomena reported in Refs. [1,2], particularly with regard to the shear rate dependence of the shift of the phase boundary when shear thinning effects are considered, and the strong dependence on the viscosity difference between components. In the form presented in this paper, the theory is not, on its own, capable of explaining disconnected miscibility gaps [1]. However, we remark that a temperature dependence of τ', comparable to that of χ, could account in a simple way for apparently disconnected regions of immiscibility. Such temperature sensitivity would arise naturally from a difference in the glass transition temperature of the two components. In a future publication, we will explore this possibility and other important consequences of the theory. We look forward to a series of carefully designed experiments with which to test the theory.

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