

Polymer Phase Separation, Kinetics of

In a simple binary system, the molecules of the two components will rearrange themselves to minimize the total free energy. When the free energy of mixing, Δf , has a region of negative curvature in terms of composition (ϕ) at a given temperature (T) and pressure (p), the system tends to phase separate into two coexisting phases (see *Polymer Mixtures, Thermodynamics of*). By following the composition pairs which define the minimum of the total free energy of mixing, Δf , (by tangent construction) as a function of temperature, the coexistence curve can be constructed. The temperature dependence of the inflection points, $((\partial^2 \Delta f / \partial \phi^2)_{T,p} = 0)$ defines the spinodal curve. Inside the spinodal curve is the unstable region, $((\partial^2 \Delta f / \partial \phi^2)_{T,p} < 0)$ where spontaneous phase separation will happen when the system is brought into this region quickly (e.g., by temperature quench or jump). The area between the coexistence curve and the spinodal curve is the metastable region, where phase separation requires a large fluctuation (*nucleation*) in order to overcome the potential barrier for further growth. One note of caution is that this interpretation is only strictly correct under the mean-field assumption.

A binary blend is defined as immiscible if it is inside the coexistence envelope, i.e., above the coexistence envelope for a system with a lower critical solution temperature (LCST), or below the coexistence envelope for an upper critical solution temperature (UCST). Thermodynamically, the system will phase separate and the dimensions of the phase separated domains will coarsen in time. In reality, the rate of coarsening depends on the system, the relative position inside the phase envelope, the interfacial modification, and other conditions used. Although an immiscible blend should continuously phase separate and coarsen with time, it is often maintained artificially at a particular stage of phase separation (in terms of morphology). Terms such as homogenized, compatibilized, and stabilized blends are often used to describe these blends or alloys (Olabisi *et al.* 1979).

1. Spinodal Decomposition

1.1 Temperature Jump Under Quiescent Condition

The following is a brief overview of spinodal decomposition studies on polymeric systems (Han and Akcasu 1992). As a binary mixture is suddenly brought from its miscible state to an unstable state, the system undergoes spontaneous phase separation. Current understanding of the dynamics of spinodal decomposition can be divided roughly into three stages: *early*, *intermediate*, and *late*.

(a) *Early stage*. At the beginning of the early stage of spinodal decomposition near the critical composition, ϕ_c , the amplitude of the composition fluctuations, $|\phi(r, t) - \phi_c|$ is sufficiently small compared with the final equilibrium composition difference, $|\phi_A - \phi_B|$, that the kinetics can be described by the Cahn–Hilliard–Cook theory (CHC), as extended for polymers (Binder 1983). In this case the time evolution of the structure factor, $S(q, t)$, after quenching into the spinodal region can be described by:

$$\frac{\partial S(q, t)}{\partial t} = -2Mq^2 \left(\left(\left(\frac{\partial^2 \Delta f}{\partial \phi^2} \right)_0 + 2\kappa q^2 \right) S(q, t) \right) + 2Mk_B T q^2 \quad (1)$$

Here M is the mobility, defined as the proportionality constant in the relationship between the interdiffusion current density and the chemical potential gradient, κ is an interfacial free energy coefficient, defined as the proportionality constant in the relationship between the interfacial free energy density and the square of the concentration gradient, and q is the wave vector. The last term is the thermal noise from the Cook representation, with an amplitude obtained from fluctuation–dissipation theory.

The solution of Eqn. (1) is:

$$S(q, t) = S_\infty(q) + (S_0(q) - S_\infty(q)) \exp(2R(q)t) \quad (2)$$

where $S_\infty(q)$ is the virtual structure factor:

$$S(q, \infty) = k_B T / \left(\left(\frac{\partial^2 \Delta f}{\partial \phi^2} \right) \right) \quad (3)$$

and

$$R(q) = -Mq^2 \left(\left(\left(\frac{\partial^2 \Delta f}{\partial \phi^2} \right)_0 + 2\kappa q^2 \right) \right) \quad (4)$$

For polymers in general, the mobility should be q -dependent. In the case where $qR_g < 1$, where R_g is the radius of gyration, M can be approximated as a constant, as is the case in most light scattering studies. The expression for κ was obtained by deGennes (1979) from a comparison of the CHC linear theory and the Random Phase Approximation (RPA) calculation of the static structure factor:

$$\kappa = \frac{k_B T}{36} \left(\frac{b_A^2}{V_A \phi_A} + \frac{b_B^2}{V_B (1 - \phi_A)} \right) \quad (5)$$

where V is the molecular volume. The interdiffusion coefficient, $D_{\text{int}} = M(\partial^2 \Delta f / \partial \phi^2)_0$, can be obtained from Eqn. (4) as the intercept in a plot of $R(q)/q^2$ versus q^2 (often referred to as a Cahn plot). The value of D_{int} is negative for the case of fluctuation growth and positive for the case of normal diffusion.

The phase separation of polymeric systems has been shown to be consistent with this linearized solution of

the mean-field formulation of spinodal decomposition. The rate of growth as a function of q , $R(q)$, the interdiffusion coefficient, D_{int} , and the virtual structure factor, $S_{\infty}(q)$, have all been obtained according to Eqns. (2)–(4).

(b) *Intermediate stage.* As the amplitude of the concentration fluctuations continues to increase, the characteristic length scale also increases with time. In general, one observes a sharpening of the spinodal peak in the scattering structure factor at q_{max} , and a gradual movement toward smaller q values. Because the amplitude of the concentration fluctuations is still changing, the interfacial distribution is also continuously sharpening, and one does not expect to observe self-similar structures. However, a universal scaling of reduced size and time has been reported in polymeric systems. In this scaling analysis, experimental results are reduced in a plot of the reduced wave number, Q_{max} , versus reduced time, τ , with:

$$\tau = t/\tau_c \quad (6a)$$

$$\tau_c = (Dq_{\text{max}}^2(t=0))^{-1} \quad (6b)$$

and

$$Q_{\text{max}}(\tau) = \frac{q_{\text{max}}(\tau)}{q_{\text{max}}(\tau=0)} \quad (6c)$$

Although this kind of scaling analysis may show some universal behavior, a direct analytical solution for the mode-coupling calculation of the time-dependent scattering structure factor of binary liquids has been obtained by Langer, Bar-on, and Miller, and extended to polymeric systems (Akcasu *et al.* 1992).

(c) *Late stage.* At the onset of the late stage of phase separation, the interface has developed into the equilibrium profile, and the compositions of the microdomains, which may be cocontinuous, have reached their equilibrium coexistence compositions, ϕ_A and ϕ_B . As the system continuously coarsens in this stage, it is presumed to follow a mechanism first suggested by Siggia. Through hydrodynamic (flow) processes, the cocontinuous structure is disrupted and coarsens with time in a self-similar fashion. Experimentally, one would expect to observe the spinodal decomposition peak intensity and position in the scattering structure factor change with time in the following manner:

$$q_{\text{max}}(\tau) \sim (\tau)^\alpha \quad (7a)$$

$$S(q_{\text{max}}, t) \sim (t)^\beta \quad (7b)$$

with

$$\beta = d\alpha \quad (7c)$$

where d is the dimensionality ($d = 3$ for a volume-filling 3D system and $d < 3$ for a less dense, fractal structure). Rigorously, in this self-similar growth regime the scattering structure factor should also be self-similar:

$$S(q, t) = (q)^{-d} \cdot f(q/q_{\text{max}}) \quad (7d)$$

$$= (q)^{-d} \cdot g(t/t_{\text{max}}) \quad (7e)$$

In other words, plots of $S(q, t) \cdot q^d$ versus q/q_{max} for various t or of $S(q, t) \cdot q^d$ versus t/t_{max} for various q should yield a universal structure factor.

1.2 Critical Temperature Shift Under Shear Flow, and Phase Separation with Shear Quench

(a) *Above critical temperature (miscible region).* In the Onuki–Kawasaki analysis for the shear rate dependence of the critical dynamics, a renormalization group calculation predicts the shear rate ($\dot{\gamma}$) dependence of the critical temperature ($T_c(\dot{\gamma})$) to be (Onuki and Kawasaki 1979):

$$\frac{T_c(\dot{\gamma}) - T_c(0)}{T_c(0)} \approx r[0.0832\varepsilon + O(\varepsilon^2)][(\dot{\gamma})\tau_c]^{1/3\nu} \quad (8)$$

where $T_c(0)$ is the equilibrium critical temperature, $r = 1 - T_c(0)/T$ is the equilibrium reduced temperature, T is the experimental temperature, $\nu = 0.63$ is the Ising correlation length exponent, and $\tau_c = \xi^2 S(0)/\Lambda_0$ is the characteristic lifetime of the equilibrium concentration fluctuations.

This prediction has been studied with a low molecular weight deuterated polystyrene/polybutadiene (PSD/PB) blend. By combining data from dynamic light scattering (DLS), and small-angle neutron scattering (SANS) with and without shear flow, Eqn. (8) has been verified. The underlying physics can be explained very intuitively. From SANS measurements of the blend under steady shear (*in situ*), the susceptibility, $S(0, \dot{\gamma})$, and the correlation length $\xi(\dot{\gamma})$, can be extracted by fitting to the properly configured structure factor calculated from Onuki–Kawasaki theory. The quantities $S(0, \dot{\gamma})$ and $\xi(\dot{\gamma})$ can be written as:

$$S(0, \dot{\gamma}) \sim \left[1 - \frac{T_c(\dot{\gamma})}{T} \right]^{-\gamma} \quad (9a)$$

and

$$\xi(\dot{\gamma}) \sim \left[1 - \frac{T_c(\dot{\gamma})}{T} \right]^{-\nu} \quad (9b)$$

where $\gamma = 2\nu$.

The break-up of large scale critical fluctuations by flow leads to a drop in the critical temperature described by Eqn. (8), and the shear rate dependence

of the susceptibility and correlation length can be written as:

$$S(0, \dot{\gamma}) = S(0)(1 + \Delta r/r)^{-\gamma} \quad (10a)$$

and

$$\xi(\dot{\gamma}) = \xi(0)(1 + \Delta r/r)^{-\nu} \quad (10b)$$

with $\Delta r = [T_c(\dot{\gamma}) - T_c(0)]/T_c(0)$. The reduced susceptibility, $S_{\text{red}} = S(0, \dot{\gamma})/S(0)$, and the reduced correlation length, $\xi_{\text{red}} = (\dot{\gamma})\xi(0)$, are then given in terms of the reduced shear rate, $\sigma = \dot{\gamma}\tau_c$, by

$$S_{\text{red}} = \xi_{\text{red}}^2 \approx \{1 + [0.0832 \varepsilon + \mathbf{O}(\varepsilon^2)]\sigma^{1/3\nu - 2\nu}\} \quad (11)$$

The quantities S_{red} and ξ_{red} are direct measures of the influence of shear on the critical fluctuations. If the flow has no effect, S_{red} and ξ_{red} are both one, as under quiescent conditions. When the flow starts to suppress the long-wavelength critical fluctuations, S_{red} and ξ_{red} begin to decrease, reflected by the decrease in the low- q scattering intensity. The intuitive explanation is that flow begins to break apart the long-wavelength critical fluctuations when the shear rate becomes comparable to the equilibrium relaxation rate of these fluctuations. This is evidenced by the fact that S_{red} and ξ_{red}^2 begin to deviate from unity when the reduced shear rate $\sigma = \dot{\gamma}\tau_c$ becomes comparable to unity, or when $\dot{\gamma} \sim \tau_c^{-1}$. It is natural that the size of the critical fluctuations would be limited by the shear for $\dot{\gamma} \geq \tau_c^{-1}$, since any component with an equilibrium lifetime greater than $\dot{\gamma}^{-1}$ will essentially be suppressed by the flow.

(b) *Below critical temperature.* When an experiment starts at a temperature below the quiescent critical temperature, $\Delta T (= T_c(0) - T)$, how the phase separated system changes in structure from two phases to one phase, and also how the critical temperature, $T_c(\dot{\gamma})$, changes as a function of shear rate are interesting and important questions. A number of different research groups have probed various aspects of multi-component systems under flow conditions using light scattering and other techniques (Nakatani and Han 1998). For polymer/polymer/solvent (e.g., polystyrene/polybutadiene blends dissolved in dioctyl phthalate (DOP)), Hashimoto has delineated five basic types of behavior under steady shear. The first two regimes are defined by zero shear or very weak shearing conditions where the sample is macroscopically phase separated (Regime I). At rest, due to density differences, the sample segregates into polystyrene-rich and polybutadiene-rich layers. An incident laser beam normal to these layers produces very little scattered light intensity. In the very weak shear regime (Regime II), the layers break up into droplets, or a highly interconnected structure which displays very little anisotropy due to flow. The light scattering

patterns in this regime are also fairly isotropic. In Regime III, the droplets become elongated and anisotropy in the scattering patterns is observed. Parallel to flow, the scattering intensity is diminished, while perpendicular to flow, the scattered intensity is constant or slightly increased. In Regime IV, the scattering intensity perpendicular to flow also becomes diminished and the scattering anisotropy is highly pronounced. This has been interpreted as the onset of remixing, where the concentration difference between the two phases is being reduced. The highly elongated droplets observed in Regimes III and IV have been referred to as a “string phase.” Finally, in Regime V, no scattered light intensity is observed except for some low intensity, critical scattering, and the sample is presumed to be homogenized on the length scales probed by light scattering.

Conversely, the shear rate dependence of the critical temperature shift, $\Delta T_c \equiv T_c(\dot{\gamma} = 0) - T_c(\dot{\gamma})$, has been studied by fluorescence microscopy images of the two-phase blend under shear flow. Using fluorophore-labeled polystyrene and unlabeled polybutadiene, the change in the fluorescence intensity ratio of the two phases under steady shear was obtained and related to the change in ratio of compositions of the two phases at different shear rates. With these fluorescence microscopy measurements at various temperatures and shear rates, it has been demonstrated that the critical temperature shift below the critical point for a UCST system can be obtained as (Yu *et al.* 1997):

$$\Delta T_c \equiv T_c(\dot{\gamma} = 0) - T_c(\dot{\gamma}) \approx (1.52 \pm 0.36)\dot{\gamma}^{0.44 \pm 0.05} \quad (12)$$

(c) *String-like domain formation and the kinetics after cessation of shear.* Kinetic studies of these polymer blends after cessation of flow have also been studied by different laboratories (Nakatani and Han 1998). In general a “spinodal ring” was observed after cessation of shear (sometimes referred to as a *shear quench* experiment) and the peak position and intensity of the peak scale as expected for the intermediate to late stages of spinodal decomposition described in previous section. However, depending on the shearing history, a coarsening, deformed two-phase structure could coexist phase separation within phase separated structures. The kinetics following a shear quench under such conditions could be quite complex. For example, with a polystyrene/polybutadiene blend, phase contrast microscopy (PCOM) indicates that after cessation of a shear which generates string patterns, the break-up of the strings into necklace-like patterns can be observed. The small bead-like domains remain aligned, giving rise to a bright scattering streak in the vorticity direction, and randomize slowly. Concurrently, a spinodal decomposition-like ring also begins to appear. The phase sep-

aration process due to the domain coarsening of the two-phase structure could be slower than the spinodal-like process. Eventually, the two processes will merge together. The string-like domain formation can be explained qualitatively by a combination of the Onuki–Kawasaki theory and the macroscopic Taylor model.

2. Nucleation and Growth

Nucleation and growth kinetics in polymer/polymer phase separation is a much less studied process. The classical theory of nucleation is based on the assumption that during the initial stages of the transformation, a few molecules rearrange themselves into droplets or nuclei that have the characteristics of the new phase. If the radius of these nuclei exceeds a certain radius to overcome the free energy barrier, then the growth of the new phase proceeds spontaneously. Some analytical theory, computer simulations and experiments have been carried out for various systems. However, the question of the initial stages of phase separation and the formation of the critical nucleus have not been clearly understood. In a more recent study of a liquid–liquid phase separation of a polyolefin system by time resolved SANS, three regimes were identified during the nucleation process: a rapid relaxation period of concentration fluctuations in response to the quench, a slow early stage of nucleation, and then a fast intermediate stage of phase separation by nucleation and growth (Lefebvre *et al.* 1999). The results are different from the predictions of the classical theories, but the cross-over from nucleation to spinodal decomposition is smooth and continuous as indicated in more recent theories.

3. Concluding Remarks

Since 1985 the phase separation behavior of binary polymer mixtures under quiescent conditions has been studied by many laboratories, with many experimental studies confirming various aspects of theoretical predictions. Of notable significance has been the verification of the CHC theory, which is a linearized mean-field approach describing spinodal decomposition. Detailed theoretical descriptions for the nonlinear, intermediate and late stages of phase separation are required beyond the scaling and mode-coupling predictions currently available and more extensive numerical simulations are also needed.

For the case of polymer blends under shear, it has been shown that the critical temperature shift as a function of shear rate can be interpreted by the theoretical model of Onuki–Kawasaki. More recent

studies of the droplet to string transition by extending this approach to the two-phase region are promising. The true shift in the phase diagram as a function of shear rate has been studied by fluorescence microscopy with limited success. Although current theories can explain these results within the moderate precision of the experiments, detailed questions such as the conditions for coupling of the flow field to the fourth power of the order parameter (critical fluctuations) in the equation of motion describing these phenomena remain unresolved.

Nucleation and growth is less understood, especially in the initial stage of nucleus formation. Due to the wide array of variables present in this subject, a large number of topics remain unexplored. For example, a wide variety of chemical additives are incorporated in commercial polymer blends and their effect on the phase separation behavior of these materials have only been investigated for a small number of specific systems. The complex relationships among shear history, sample temperature, additive concentration, homopolymer molecular weights, and viscosity is quite evident. While some systematic studies have been initiated, there is still a substantial amount of work remaining before a coherent understanding of the phase separation kinetics in multicomponent systems can be achieved.

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