

Critical Temperature Shift and Mixing in Polymer Blends Under Simple Shear Flow

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Small Angle Neutron Scattering (SANS) has been used to measure the influence of shear flow on a polymer blend near critical point. When combined with dynamic light scattering measurements, data reveal that the long-range critical fluctuations begin to break apart which is related to the decrease of critical temperature caused by the flow. This can be compared with the theoretical predication of Onuki and Kawasaki. For phase separated blends, homogenization occurs via repeated domain fragmentation, which gives way to distinct patterns in the strong shear limit. Data for a variety of systems collapse onto universal scaling curves that are in good agreement with modern theories.

KEYWORDS: small angle neutron scattering, critical temperature shift, polymer blends, pattern formation, shear on mixing

§1. Introduction

The morphology of polymer blends under shear is of great importance both in the fundamental understanding and in the practical application. There is a remarkable degree of complexity surrounding polymeric fluids under shear, and a universal description is clearly a challenging task. For blends above but near the critical point of unmixing, a useful starting point is the mode-coupling renormalization-group (MCRG) theory of a simple binary fluid under shear.^{1–3)} Although the shear response of small-molecule mixtures is consistent with the MCRG theory, the slow relaxation times characteristic of macromolecular systems permit a unique and rigorous test. Small-angle neutron scattering has

been a powerful tool for such studies, and has provided detailed comparison between theories and experiments in the miscible or "one-phase" region of the phase diagram.^{4,5)} On the other hand, the response of the blend in the unstable or "two-phase" region is of greater interest from a practical perspective. The "in-situ" combination of light scattering and digital-video microscopy is an extremely powerful tool for studying the morphology of polymer blends under shear^{6–9)} in this phase separated region. We will present our results and analysis on the shear effect with the use of a low molecular mass polystyrene/polybutadiene (PS/PB) blend above critical temperature and also the results of PS/PB blends with a combination of different molecular masses and solvent composition in the two phase region.

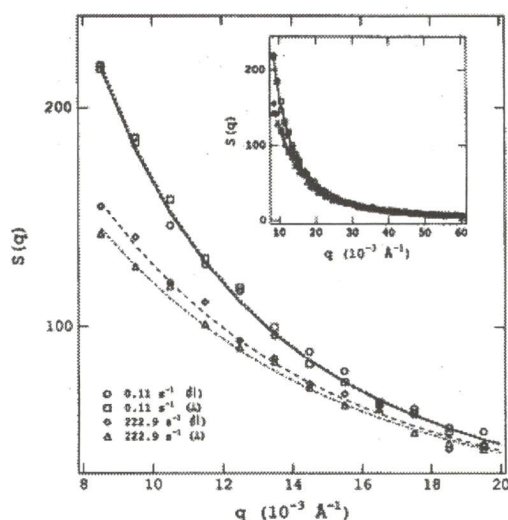


Fig. 1. The low- q structure factor $S(q, \gamma)$ measured along ($\parallel$) and normal ($\perp$) to the flow direction in both the weak and strong shear limits at 42 °C. Over most of the q -range, the scattered intensity (insert) is unaffected by the shear rates used in this study.

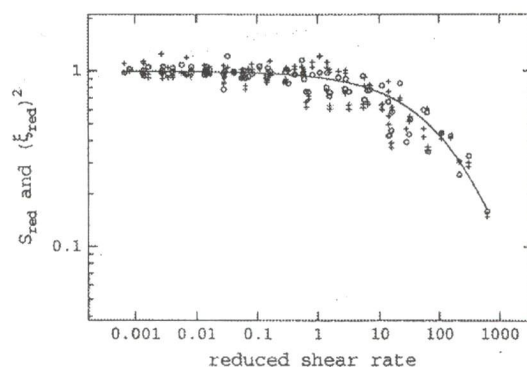


Fig. 2. The square of the reduced correlation length and the reduced susceptibility as a function of reduced shear rate for a deuterated polystyrene/polybutadiene blend. The solid line is the behavior predicted by the Onuki-Kawasaki theory to the zeroth order ϵ expansion, $0(\epsilon)$, over six decades in reduced shear rate, with no free parameters.

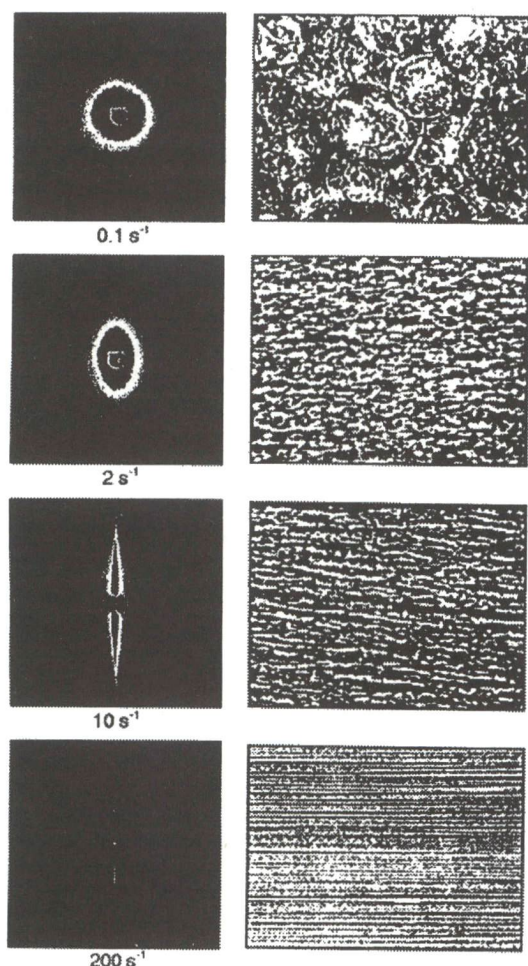


Fig.3. Light scattering/micrograph pairs as a function of shear rate for a coexisting low-molecular-weight [60/40 PS/PB ($3.4 \times 10^3/3 \times 10^3$)] critical blend. The temperature of 132.7 °C is 1.5 K below the equilibrium T_c . Stabilized in the weak-shear limit, droplets of the minority phase first elongate and then fragment repeatedly, eventually giving way to a string-like morphology in the strong shear limit. The extreme anisotropy of the domains becomes inverted in q space. The flow direction is the horizontal direction, and the vorticity direction is the vertical direction of the graph.

§2. Results and Discussion

The structure factor $S(q)$ can be measured by SANS with and without shear. The quiescent result can be used to extract either the susceptibility, $S(q=0)$, or the correlation length, ξ . This correlation length can be combined with dynamic light scattering measured decay rate of concentration fluctuations, Γ_c ($\Gamma_c = D_c q^2$) to obtain the characteristic lifetime of the order parameter fluctuations ($\gamma_c = \xi^2/D_c$). Again the concentration fluctuations can be measured by SANS under shear flow. A typical shear suppression of concentration fluctuation is shown in Fig. 1. In the quiescent or equilibrium limit, the MCRG model reduces to Model H in the Hohenberg-Halperin classification scheme.¹⁰⁾ The effect of shear appears in the equation of motion for the order parameter, which represents local deviations from the uniform composition. The essential physics of the mode-coupling argument lies in the hydrodynamic coupling between the

order parameter and the velocity field. Long-wavelength composition fluctuations are transported and deformed by the viscous motion of the fluid, and the flow stabilizes an anisotropic steady state away from thermodynamic equilibrium. In polymer blends, critical fluctuations lead to a crossover from mean-field to Ising behavior, and the window around T_c where mean-field theory breaks down can be quite large. The subtle interplay between mode-coupling and Ising-critical effects is the foundation of the MCRG description, which predicts a suppression of the critical temperature by the shear. The flow would have a mixing effect on a two-component fluid is intuitive, although the details of the theory itself are quite complicated. The response of the mixture depends on how large the shear rate, γ , is compared to $1/\tau_c$, where τ_c is the order-parameter relaxation time which can be measured as described above. This makes it convenient to define a reduced, dimensionless shear rate $s = \tau_{c0} \gamma$, the resembles of Deborah number in appearance. For binary fluid that exhibits critical fluctuations, SANS gives a correlation length and susceptibility, $\xi(\gamma)$ and $S(q)$ respectively, that reflect the shear-induced shift in T_c . Reducing these quantities by their equilibrium values and plotting them as a function of the reduced shear rate, s , gives a universal scaling curve containing no free parameters. This can be demonstrated in low-molecular-mass as shown in Fig. 2, and also in diluted high-molecular-mass⁵⁾ blends and reveals the intuitive result that composition fluctuations are suppressed when $s > 1$. The relaxation time, correlation length, and susceptibility all become quite large at the critical point, where long-wavelength structures are easily sheared apart by the flow. In the two phase region, a cross over from droplets to strings has been observed by

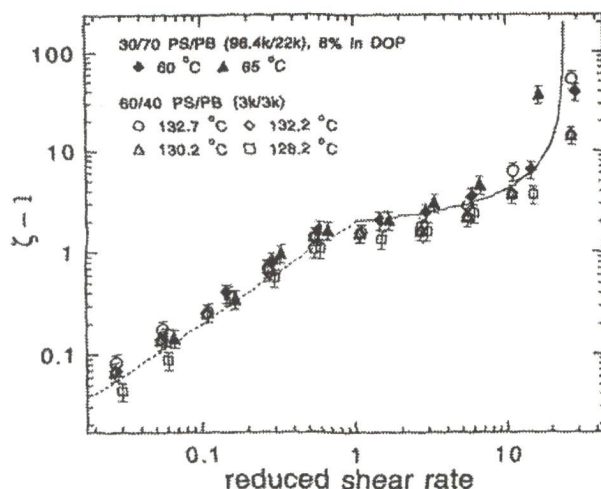


Fig.4. Log-log plot of the dimensionless deviation from isotropic droplets as a function of reduced shear rate, or Deborah number, for a variety of polymer mixtures in the vicinity of a critical point. The dashed line represents the weak-shear (Taylor) limit, while the solid line is the crossover to strong-shear. The onset of nonclassical behavior corresponds to the reduced shear rate equals to one, which is when the droplets, on average, start to break ζ is the aspect ratio of the droplet.

the shear light scattering/optical microscopy techniques. This is demonstrated in Fig. 3. As a first approximation, we consider a single incompressible droplet of average size and assume that it breaks into two identical fragments. The aspect ratio of an individual droplet can be described by an expansion of Taylor model, but with a shear-dependent surface tension as a consequence of the MCRG theory. The droplet dimensions after n breaking transitions can be expressed in terms of n , the initial droplet size, and the reduced shear rate, $s = \tau_{e0} \gamma$, where the bare stress-relaxation time τ_{e0} , is determined from a fit of the average aspect ratio vs. the shear rate in the weak-shear limit before the droplets, on average, start to break. This description is leading-order in the sense that it neglects shear thinning, ignores the viscosity difference between droplet and matrix, assumes mean-field breaking transitions, ignores droplet interactions, and greatly oversimplifies the breakup of an isolated droplet. However, the droplet to string crossover for polymer blends at different temperatures and solvent concentrations can be captured very nicely in a universal representation. This is shown in Fig. 4.

Close to the critical point, the response of the mixture can be explained by combining classical hydrodynamics^{11,12)} with the MCRG theory. Well into the equilibrium two-phase region of high-molecular-weight systems, however, such a description appears to break down in a way that may have implications for the flow-induced blending of polymers.

§3. Conclusion

In this presentation, data obtained by dynamic light scattering, and by small angle neutron scattering with and without shear for a polystyrene/polybutadiene blend, have been compared with the MCRG theory. The shear induced shift of phase diagram is demonstrated.

In the two phase region, droplet to string transition has been observed. A simple combination of the classical hydrodynamic theory and the above MCRG theory has been used to explain this droplet to string crossover. For immiscible systems with large differences in viscosities, the shear deformation could be very much changed due to hydrodynamic effects. Polybutadiene and polyisoprene blends with different viscosity ratios have been used in such study. Droplet deformation, string formation, mixing/de-mixing, and phase inversion can be observed under different quench depth, and shear conditions. Understandings in these directions are important fundamentally as well as application wise.

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