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Real-time observation on deformation of bicontinuous phase under simple shear flow

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The transient shear deformation of phase-separated bicontinuous structures has been investigated by a real time optical microscopy and a small-angle light scattering technique. It is found that, under simple shear flow, the domains are affinely elongated for the shear strain $\gamma>1$, and the size distribution of the domains is broadened along the flow direction due to the shear-induced coalescence; while in the perpendicular direction, both the average size and the size distribution of the domains remain almost unchanged, but the correlation of the concentration fluctuations is enhanced. The experimental observations are further confirmed by computer simulation. [S1063-651X(98)51508-5]

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Spinodal decomposition (SD) dynamics of mixtures has been extensively studied during the last few years, due to its great importance for both nonequilibrium statistical physics and technical applications. Although there are many interesting questions open, the basic features of SD are, however, well understood. A series of scaling properties have been observed. In the late stage of SD, the domain growth is governed by a power law of the form $q_m(t)\sim t^{-\alpha}$, where t is the time, $q_m(t)$ is the magnitude of the scattering wave vector at the maximum of the scattering function and is the reciprocal length of the system related to the average domain size Λ_m by $\Lambda_m=2\pi/q_m$, and α is the growth exponent [1].

When a shear flow acts on the system simultaneously with SD, a number of intriguing effects are observed [2–5]. Experimental observations [6] on polymer mixtures and computer simulations [7] have shown that highly elongated domains are formed in the course of domain growth even in very weak shear. Under strong shear, a string phase of phase-separating polymer mixtures in steady state [8,9] was observed. However, no unambiguous information has yet been gained on the transient domain deformation in the bicontinuous state under shear flow. In order to get a deeper insight into the transient shear deformation of phase-separated bicontinuous structures, we have conducted an *in situ* real space analysis of the domain structures by optical microscopy (OM) and a reciprocal space analysis by small-angle light scattering (SALS). The experimental observations are further confirmed by computer simulation based on time-dependent Ginzburg-Landau (TDGL) equation.

The polymer blend consists of polystyrene (PS) and poly(vinyl methyl ether) (PVME). The molecular weight M_n of PS and PVME are 38 000 and 95 000 g/mol, the corresponding heterogeneity indices of PS and PVME are $M_w/M_n=1.5$ and 2.8, respectively. The phase diagram was measured by the cloud-point method, and showed that it is a system of lower critical solution temperature, with a critical composition of 18 wt. % PS and a critical temperature of 108 °C. The blend of 50/50 wt. % composition, with the phase-separation temperature of 114 °C, were used in the shear experiment.

The shear is introduced by a rectilinear shear apparatus constructed in our laboratory, which is similar to the design of Larson and Mead [10]. The cell is transparent and the He-Ne gas laser beam ($\lambda_0=632.8$ nm, 5 mW) is normal to the cell plane. The scattering was imaged on a screen placed normal to the incident beam, whose intensity distribution, $I(\mathbf{q})$, was captured by a charge-coupled-device (CCD) camera. The magnitude of scattering wave vector $\mathbf{q}$ is defined as $q=(4\pi/\lambda)\sin(\theta/2)$, where θ and λ are the scattering angle and the wavelength of the laser in the medium. The transmission light micrographs (LEITZ, Orthoplan) were also taken in the cell plane. The polymer blend was filled between the two glasses with a gap distance of about 20 μm. The homogeneous sample was first stayed in 105 °C for 12 h and then jumped to 125 °C rapidly. After 4 min of the SD without shear, well-defined isotropic bicontinuous domains were evolved. Then the shear flow was turned on with the shear rates $\dot{\gamma}$ of 0.5 and 2.0 s^{-1}. The transient domain deformation under the simple shear flow was followed *in situ* by the time-resolved OM and SALS.

Figure 1 shows SALS patterns for a shear rate of $\dot{\gamma}=0.5\ s^{-1}$. The different shear strains, γ, at which the pictures were taken, are indicated under each figure. Here the shear is applied along the x direction (the flow direction), the velocity gradient direction is defined as the y axis, and the z direction is referred to as the perpendicular direction. As expected, in the absence of shear flow, the scattering pattern is a typical spinodal ring, which means the phase-separated structure is isotropic. Once the flow field is applied, the scattering patterns are deformed anisotropically and take on the shape of ellipse with the minor axis parallel to the flow direction. It is notable that the development of the elliptical patterns is caused only by a compression of the scattering intensity along the flow direction and is not accompanied by an elongation along the perpendicular direction. This effect is demonstrated in Fig. 2, where the scattering vectors q_m in the shear and perpendicular directions are plotted against shear strain. It is clearly seen that, for $\gamma>1$, the structure deforma-

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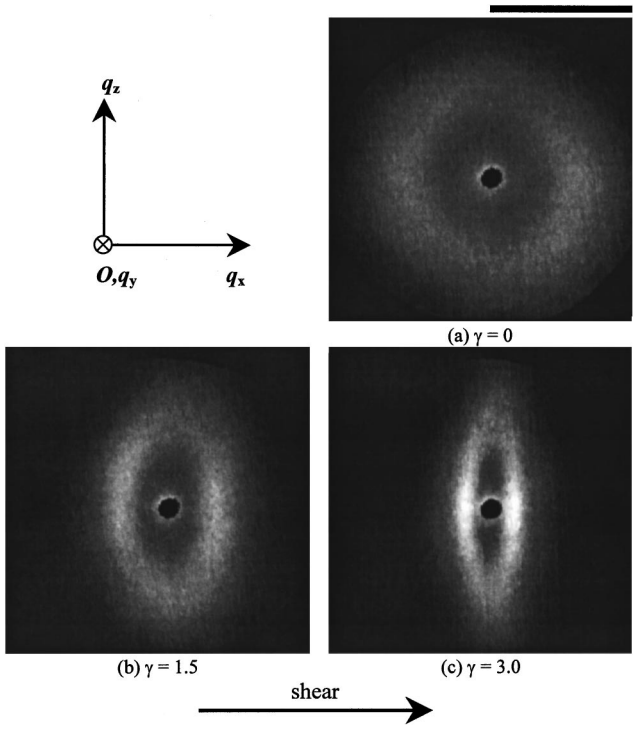

FIG. 1. SALS patterns obtained *in situ* by the CCD camera in the SD process of the PS/PVME blend at various shear strain: (a) 0.0, (b) 1.5, and (c) 3.0, with a shear rate of $\dot{\gamma}=0.5\ \mathrm{s}^{-1}$ at 125 °C. The black bar corresponds to $q=6\ \mu\mathrm{m}^{-1}$.

tion along the flow direction obeys a power law as $q_{mx} \propto \gamma^{-1}$. In the late stage SD, the growth rate Γ of the domains is defined as $\Gamma=l^{-1}dl/dt$, where l is the characteristic length and is given by $l=Kt$. The value of K, measured from the time evolution of the scattering of the phase-separating blend at 125 °C in the absence of shear flow, is about 0.008 $\mu\mathrm{m\ s}^{-1}$. The average size of the domains is about 2 μm when the shear flow was turned on. Then, the domain growth rate Γ is estimated as 0.004 s^{-1}, which is much lower than the shear rates $\dot{\gamma}=0.25$ and 2.0 s^{-1}, hence, the domain growth via SD during shearing can be ignored. Therefore,

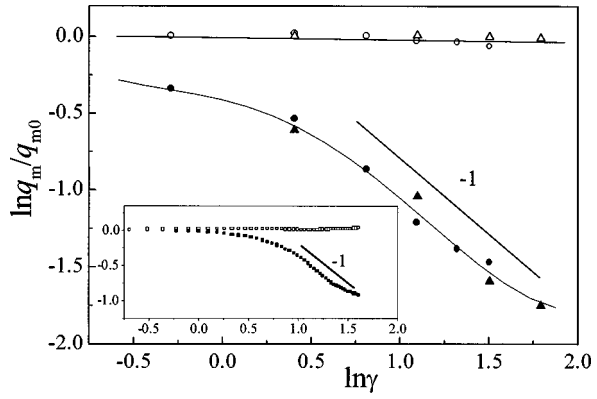

FIG. 2. Shear-strain dependence of q_m with various shear rate $\dot{\gamma}$: ●○, 0.5 s^{-1}; ▲△, 2 s^{-1}. The closed and open symbols correspond to the flow and perpendicular direction, respectively. In the inset, the simulated shear-strain dependence of q_m with the reduced shear rate $S\equiv\dot{\gamma}/M=0.01$ is shown. The simulation is carried out on a $128\times128\times16$ lattice.

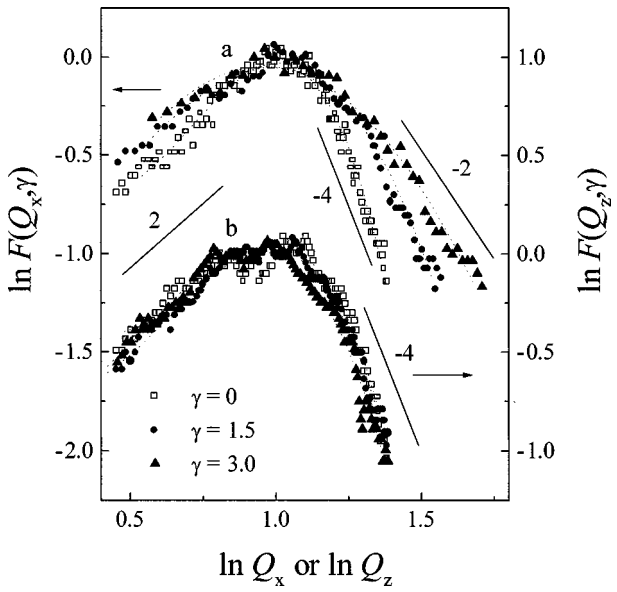

FIG. 3. Plot of the normalized scattering intensity $F(Q,\gamma)$ as a function of normalized scattering vector Q at various shear strain γ: □, 0; ●, 1.5; ▲, 3.0. (a) Normalized scattering intensity along the flow direction; (b) Normalized scattering intensity along the perpendicular direction.

the exponent -1 reflects that the domains are affinely elongated along the flow direction. On the other hand, q_{mz} is independent of the shear strain, indicating that the average size of the domains in the perpendicular direction is almost unchanged.

It is well known by now that the domain growth is dynamically self-similar and can be described in terms of a scaling ansatz in the late stage SD in the absence of shear. In many experiments, this property has been investigated by using the scaled scattering function. However, under simple shear deformation, the scattering intensity depends on the direction of the wave vector, it is hence impossible to obtain the invariant of scattering $I(\mathbf{q},\gamma)$, which is needed in the normalization of $I(\mathbf{q},\gamma)$. Therefore, following Matsuzaka *et al.* [11], we normalize $I(\mathbf{q},\gamma)$ as $F(Q,\gamma)=I(\mathbf{q},\gamma)/I(\mathbf{q}_m,\gamma)$, where $Q=\mathbf{q}/|\mathbf{q}_m(\gamma)|$ and $\mathbf{q}_m$ is the wave vector along $\mathbf{q}$ at which the maximum intensity is detected. Shown in Fig. 3 are the shear strain dependencies of the normalized scattering intensity as a function of the normalized scattering vector $\mathbf{q}$ along the q_x and q_z axes. It is seen that in the absence of the shear, both $F(Q_x,0)$ and $F(Q_z,0)$ obey Porod's law, i.e., $F(Q)\sim Q^2$ for small Q, and $F(Q)\sim Q^{-4}$ for large Q. However, as the shear flow is applied, $F(Q_x,\gamma)$ takes the form of $F(Q)\sim Q^{-\varepsilon}$ for large Q and the exponent $\varepsilon(\gamma)$ is slightly dependent on the shear strain γ, indicating that the shear deformation makes the size distribution of the domains along the flow direction broader. It is worth noting that similar violation of the scaling under simple shear flow was also found by Chan, Perrot, and Beysens [12] in a small molecular mixture of isobutyric acid and water. On the contrary, $F(Q_z,\gamma)$ is invariant with the shear flow, indicating that the simple shear deformation have no effect on the domain size distribution along the perpendicular direction. From the above discussions, we conjecture that, in the flow direction, the shear flow has two effects: first, it affinely elongates the domains; second, it promotes the col-

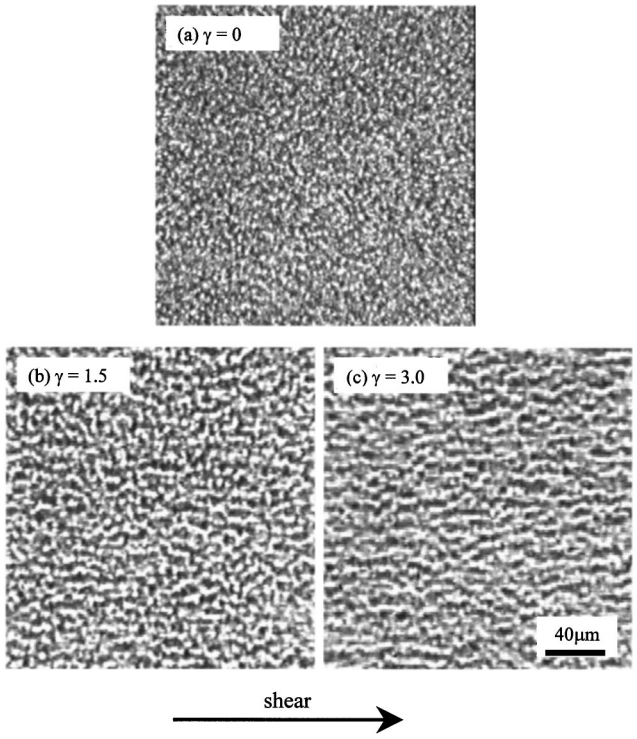

FIG. 4. Optical micrographs of PS/PVME blend captured at various shear stain: (a) 0.0, (b) 1.5, and (c) 3.0. The shear rate is $0.5\ s^{-1}$.

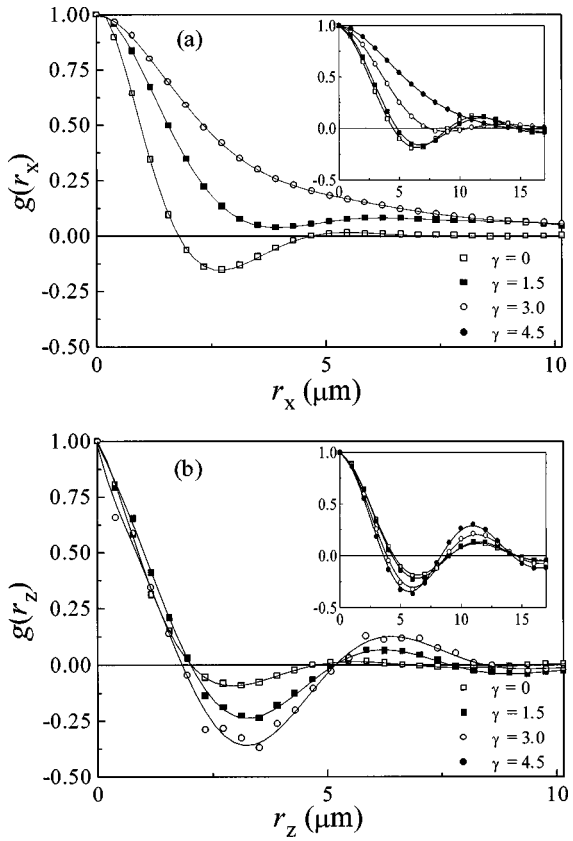

FIG. 5. Normalized pair correlation functions calculated from the optical micrographs of PS/PVME blend at various shear strain with $\dot{\gamma}=0.5\ s^{-1}$ at 125 °C. (a) Correlation functions in the flow direction; (b) Correlation functions in the perpendicular direction. Insets: The corresponding simulated pair correlation functions with $S=0.01$. The simulation is carried out on a $128\times128\times16$ lattice, and the unit of r_x and r_z in the insets is one lattice spacing.

lisions and thus coalescences of the domains smaller than $2\pi/q_m$, and this is responsible for the broadening of the domain size distribution along this direction. By using the time-resolved OM, these two effects will be further illustrated later. Here, we should emphasize that we are not dealing with the deformation of droplets, but the deformation of a phase-separated bicontinuous morphology, the elongation of the domains along the flow direction will not consequently cause the contraction of these domains in the perpendicular direction. Actually, in the perpendicular direction, both the domain size and size distribution are not affected by the shear flow.

In Fig. 4, the optical micrographs of the phase-separated PS/PVME blend, captured by a CCD camera at $\gamma=0$, 1.5, and 3.0, are shown. After the phase separation has proceeded for about 4 min, bicontinuous phases typical of SD are observed [Fig. 4(a)]. As the shear is applied, the bicontinuous phases are stretched and coalescenced, upon shear, in the flow direction, while the size scale remains almost unchanged in the perpendicular direction. At larger shear strain, the domains align along the flow direction [Fig. 4(c)].

In order to quantitatively analyze the optical micrographs obtained above, we use the digital image analysis (DIA), which was first proposed by Tanaka, Hayashi, and Nishi [13] to study the phase separation of polymer blends. In our case, we define the normalized intensity at $\mathbf{r}$ in a micrograph as the local concentration $\varphi_A(\mathbf{r})$, and the order parameter $\Psi(\mathbf{r})$ is defined as the deviation of $\varphi_A(\mathbf{r})$ from the average concentration, $\bar{\varphi}$, i.e., $\Psi(\mathbf{r})=\varphi_A(\mathbf{r})-\bar{\varphi}$. We then calculate the pair correlation function defined as $G(\mathbf{r})=\Sigma_{\mathbf{r}'}\langle\Psi(\mathbf{r}')\Psi(\mathbf{r}'+\mathbf{r})\rangle$. Figure 5(a) shows the normalized pair correlation functions, $g(r_x)=G(r_x)/G(0)$, in the flow direction at various shear strain. In the absence of shear flow, the characteristic damped oscillatory behavior of $g(r_x)$ for the conserved order parameter is seen. Once the shear flow is imposed, as expected, the characteristic length increases. However, the more interesting feature of $g(r_x)$ is that the oscillation is almost absent with the increase of the shear strain, and the magnitude of the correlation function is very small for large r. We conjecture that the broader domain size distribution along the flow direction may cause the loss of the well-defined characteristic length, and thus smears out the oscillation of $g(r_x)$. While for the correlation function in the perpendicular direction, $g(r_z)$, another feature, appears. It is clearly seen from Fig. 5(b) that the characteristic length remains almost constant but the amplitude of the oscillation of $g(r_z)$ increases with increasing the shear strain. This indicates that the correlation of the concentration fluctuation in the perpendicular direction increases with the increase of shear strain. We believe that most of the domains are regularly aligned parallel to the flow direction causes the correlation enhancement of the concentration fluctuations in the perpendicular direction.

Additionally, we have performed a cell-dynamical simulation (CDS) [14], based on the TDGL equation, to qualitatively confirm the above experimental findings. Under a macroscopic flow field, the dynamics of the order parameter $\Psi(\mathbf{r},t)$ is assumed to be the standard TDGL equation with a convective term, which reads [7]

$$\frac{\partial \Psi(\mathbf{r},t)}{\partial t} = -\mathbf{v}\cdot\nabla\Psi(\mathbf{r},t) + M\nabla^2 \frac{\delta F[\Psi(\mathbf{r},t)]}{\delta\Psi(\mathbf{r},t)}, \qquad (1)$$

where $\mathbf{v}=(\dot{\gamma}y,0,0)$ is the velocity of flow field, M is the mobility, and F is the free energy functional of binary polymer mixtures.

As a measure of the characteristic wave vector, the first moment of the strain-dependent structure function $S(\mathbf{k},\gamma)$, $\langle\mathbf{k}\rangle=\Sigma_{\mathbf{k}}S(\mathbf{k},\gamma)/\Sigma_{\mathbf{k}}S(\mathbf{k},\gamma)$, is calculated after the shear flow is applied. The result is shown in the inset of Fig. 2. It is found that the growth law of $\langle k_x\rangle$ is given by $\langle k_x\rangle \propto \gamma^{-1}$ for $\gamma>1$, while $\langle k_z\rangle$ is almost independent of the shear strain. These behaviors of $\langle\mathbf{k}\rangle$ are in good agreement with the experimental results, demonstrated in Fig. 2. The calculated pair correlation functions $g(r)$ along and perpendicular to the flow direction are shown in the insets of Figs. 5(a) and 5(b), respectively. Qualitatively, these behaviors of $g(r)$ clearly resemble the experimental results. In this simulation, we have not carefully adjusted the parameters and just choose the same set of parameters as in Ref. [14]. Since the TDGL formalism is simply a model equation that describes the phase separation dynamics of binary fluid mixtures, quantitative agreement with the experimental results is not expected.

In summary, we have investigated the transient deformation of bicontinuous structures by SALS and OM combined with DIA. We found that, together with affinely elongating the domains along the flow direction, the simple shear flow promotes the collisions of the domains, which shows some kind of shear-induced coalescence in the flow direction, and hence makes the size distribution of the domains broader. However, in the perpendicular direction, both the average size and the size distribution of the domains remain almost unchanged, but the correlation of the concentration fluctuations is enhanced because of the aligning of the domains along the flow direction. For comparison, we also carried out computer simulation based on TDGL equation and found qualitative agreement between the experiment and theory.

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