Rheological Response from Phase-Separated Domains as Studied by Shear-Microscopy

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Abstract: The relation between rheological properties and phase-separated structures of polymer blend solutions is investigated by using shear microscopy method to obtain deeper insight into the mechanism of steady state formation under shear flow. The time dependence of viscosity and morphology is observed after a stepwise increase of shear rate. We have found that a large strain needs to burst the initial domains, time of which relates with a relaxation time of the initial domains.

Indroduction

The effects of shear flow have been attracting growing attention in various fluid systems. A number of intriguing dynamical effects have been observed for phase-separated mixtures under shear flow.[1-3] In this situation domains grow due to thermodynamic instability, but they break into smaller domains by the flow field. As a result, a stationary phase-separated structure, i.e., a steady state structure, is achieved at a constant shear rate $\dot{\gamma}$, due to a dynamical balance between the two mechanisms of domain growth and breakup.[1,4] In order to clarify the mechanism of the steady states formation, we focus on the kinetic pathway from one steady state to another steady state. We also try to clarify the relation between phase-separated domain structures and their rheological response under shear flow.

Experimental

We use dioctylphthalate (DOP) solutions of binary mixtures composed of polystyrene (PS) and polybutadiene (PB) mixed in a ratio of 50:50 by weight. DOP is a common solvent for both PS and PB. The solutions contain total amount of polymer by 6.0 wt%. The PS had a weight-average molecular weight ($\overline{M}_w$) of 2.15×10^5, and the PB had an $\overline{M}_w$ of 3.13×10^5. This is a semidilute solution with concentration c satisfying $c/c^* \cong 4$, c^* being the overlap concentration, where the entanglement effects are not yet severe. The mixture in quiescence is macroscopically phase-separated above and below an interface due to gravity.

Measurements of shear viscosity η were carried out with ARES-FS (Rheometric Scientific Co. Ltd.) by using a cone-plate geometry with 50 mm diameter and 0.04 radian of

cone angle. Transmission light microscope observations were performed by specially modified RMS-800 (Rheometric Scientific Co. Ltd.) by using a cone-plate geometry made of quartz with 80 mm diameter and 1.0° of cone angle.[5]

Results

We first imposed shear flow of shear rate $\dot{\gamma}_0 = 0.01\ s^{-1}$ to the sample for 1 hour at 30 ℃ to develop an initial steady state domain, and then rapidly increased the shear rate to $\dot{\gamma}_1 = 0.2\ s^{-1}$, which is referred to as "shear-jump" hereafter. Then we started to take a shear viscosity η as a function of time t, where $t = 0$ is defined at a moment of shear-jump. Shear viscosity η is plotted against a strain magnitude $\dot{\gamma}_1 t$ after shear-jump, as shown in Fig. 1. Upon increasing $\dot{\gamma}_1 t$, η first increases until $\dot{\gamma}_1 t = 2$, then decreases until $\dot{\gamma}_1 t \sim 50$, and increases again with approaching a constant value. This behavior was observed independent of $\dot{\gamma}_0$ and $\dot{\gamma}_1$ covered in the present study provided that $\dot{\gamma}_1$ is sufficiently larger than

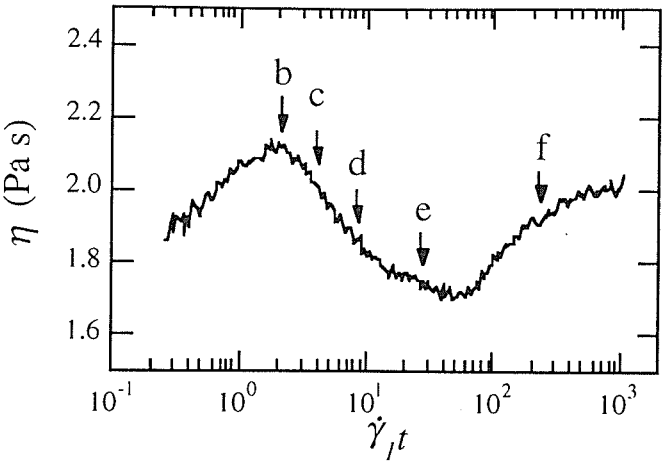

Fig. 1 Shear viscosity η is plotted against $\dot{\gamma}_1 t$ after shear-jump from $\dot{\gamma}_0 = 0.01\ s^{-1}$ to $\dot{\gamma}_1 = 0.2\ s^{-1}$. Arrows with alphabets correspond to the micrographs shown in Fig. 2.

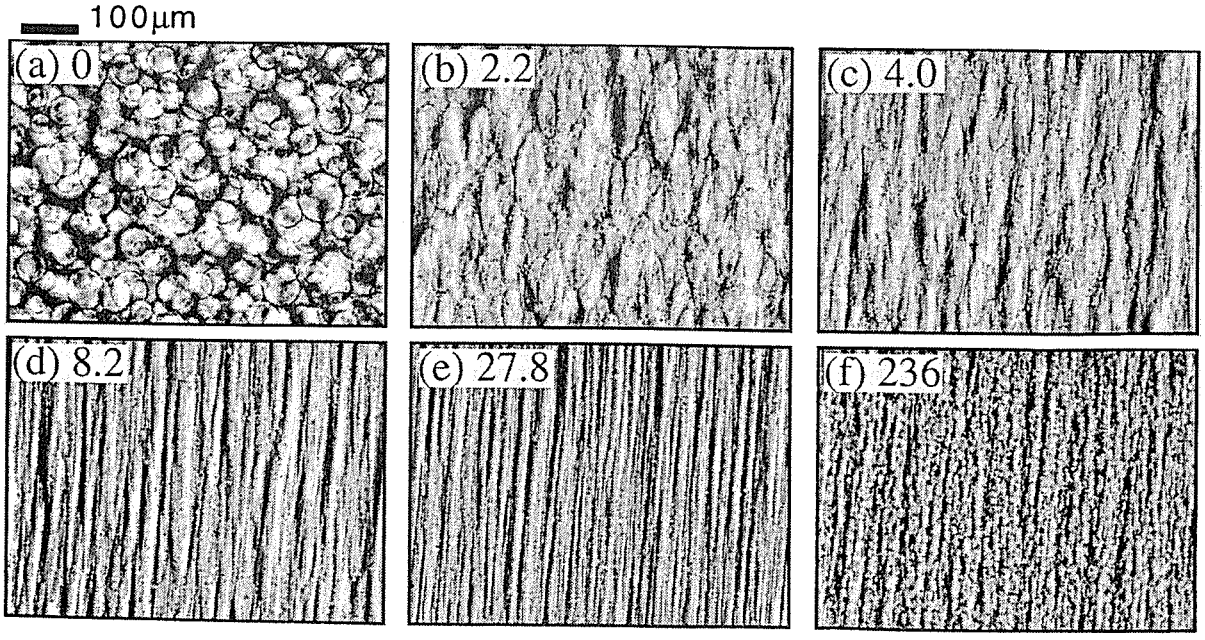

Fig. 2 Transmission light micrographs of phase-separated structures after shear-jump from $\dot{\gamma}_0 = 0.01\ s^{-1}$ to $\dot{\gamma}_1 = 0.2\ s^{-1}$. The number attached to each micrograph indicates $\dot{\gamma}_1 t$. The flow direction is vertical.

$\dot{\gamma}_0$, but not observed for homopolymer solutions of both PS and PB having the same polymer concentration as the solution of the polymer mixture, indicating that they come from phase-separated domains.

To specify the origin of the viscosity behavior in Fig. 1, we observed time evolution of structures by transmission optical microscopy with the same shear history as shear viscosity measurements. Fig. 2 shows an evolution of structures on micrographs after the shear-jump from $\dot{\gamma}_0 = 0.01\ s^{-1}$ to $\dot{\gamma}_1 = 0.2\ s^{-1}$ as a function of strain $\dot{\gamma}_1 t$.

Fig. 1 and Fig. 2 reveal that η has an overshoot in the process of domain elongation resulting in the formation of a transient string phase and that η increases again when strings burst into a lot of fragments. We emphasize that these results cannot be explained by the previous theoretical study[6] on the same phenomena as studied here, because this is based on the 2D computer simulation without hydrodynamic interactions. This shows that it is necessary to perform the computer simulation under the conditions reflecting the experimental situations more closely.

Discussion

We try to interpret first the behavior in the small deformation regime, i.e., an early stage after the shear jump before reaching steady state, $\dot{\gamma}_1 t < 10$. We can think of the characteristic (relaxation) time, τ_0, for the initial domains existing at $\dot{\gamma}_0$, which is given by $\tau_0 \sim \dot{\gamma}_0^{-1}$. We can think of the characteristic deformation time, τ_d, by shear, as well, for the higher shear rate $\dot{\gamma}_1$ which is given by $\tau_d \sim \dot{\gamma}_1^{-1}$. After imposing shear of $\dot{\gamma}_1$ to the system, in the time scale t satisfying $t \ll \tau_d$ or $\dot{\gamma}_1 t \ll O(1)$, the domains are not significantly affected by the shear but they are rather affected by thermodynamic situations. However in the time scale $t \geq \tau_d$ or $\dot{\gamma}_1 t \geq O(1)$, shear dominantly controls the structures and attains the dynamical equilibrium as already discussed. For the shear jump experiment defined above, we have $\dot{\gamma}_1 > \dot{\gamma}_0$, i.e., $\dot{\gamma}_1^{-1} < \dot{\gamma}_0^{-1}$, giving rise to $\tau_d < \tau_0$. Thus just after applying the shear jump, the initial domain existing at $\dot{\gamma}_0$ cannot relax during the deformation time τ_d and consequently the initial domains at $\dot{\gamma}_0$ is deformed in the time scale of $\tau_d < t < \tau_0$ or $O(1) < \dot{\gamma}_1 t < O(\dot{\gamma}_1/\dot{\gamma}_0)$ under the continuing shear of $\dot{\gamma}_1$, where we define reduced time $\tilde{t}_1$ at shear rate $\dot{\gamma}_1$ by $\tilde{t}_1 \equiv t/\tau_d \sim \dot{\gamma}_1 t$.

We next consider the regime of $t \gg \tau_d$ or $\dot{\gamma}_1 t \gg O(1)$ where the overshoot in η has already been experienced. After the overshoots and η reaching a minimum, η increases again

due to the breakup of the transient string-like structures. The breakup time τ_b, at which the upturn of η begins, depends on $\dot{\gamma}_0$: τ_b decreases with increasing $\dot{\gamma}_0$. This means that the larger the size of the initial domains the longer time it takes to break the initial domains. The breakup should relates with the lifetime of the initial domains, which may be determined by τ_0. Therefore, η after the overshoot may have a relation with the reduced time $\tilde{t}_0 \equiv t/\tau_0 \sim \dot{\gamma}_0 t$.

It is difficult at this stage to fully understand what controls τ_b because τ_b relates to the formation and the stability of transient string-like structures under simple shear flow. This is also important to explain the appearance of the string phase as a steady state structure under simple shear flow. As a classic result, a string-like structure is unstable against long wavelength undulations in the absence of shear flow. However, steady shear flow can form a stable string phase in a strong shear regime,[4] implying that the shear flow suppresses the instability of the structures. This effect makes the string-like structures stable transiently in the present case as shown in Fig. 2.

Conclusion

We have shown the time evolution of structures after the shear-jump in relation to their rheological behavior in order to obtain a deep insight into the mechanism of a steady state formation. We have shown that the extremely elongated domains are formed transiently in this process, which is important to understand the stability of string phase formed at steady state at strong shear regime. We have found that the time evolution of the phase-separated domains and the resulting change in η relates to the two characteristic times: the shear deformation time $\tau_d \sim \dot{\gamma}_i^{-1}$ and the relaxation time of the initial domains $\tau_0 \sim \dot{\gamma}_0^{-1}$.

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