Shear-Induced Novel Structure in Phase Separated Polybutadiene/Polyisoprene Blends

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Introduction

Shear-induced phase formation or inversion in two-phase polymer blends is a key parameter for the control of morphology and properties in many practical areas [1,2]. Phase inversion is traditionally associated with emulsions in which there are two phases: dispersed and continuous. When the dispersed phase is converted into continuous phase due to the component concentration, temperature, and/or shear forces, it is known as phase inversion. Paul and Barlow [3] and Jordhamo et al [4] proposed an empirical equation to predict the phase inversion composition, which was later extended by Miles and Zurek [5] as:

$$\alpha = \frac{\phi_A}{\phi_B}\frac{\eta_B(\dot{\gamma})}{\eta_A(\dot{\gamma})} \qquad (1)$$

where ϕ_i is the volume fraction of component i (i = A or B) in binary mixtures and η_i represents the viscosity of component i at a given shear rate ($\dot{\gamma}$). This equation implies that the viscosity and composition ratio of the two components determine phase inversion point. If α is higher than 1 the B-rich phase is dispersed phase, but if α is lower than 1 the A-rich phase is dispersed. In contrast, if the viscosity ratio of the components is balanced with the composition ratio ($\alpha \approx 1$), the phase inversion may be occurred under quiescent or shear conditions.

Phase inversion or formation in two-phase polymer blends is not as well understood as it is in emulsions. The morphology of polymer blends is affected by blending conditions, the composition of blend, the viscoelastic properties of both phases, and the interfacial tension between the components. The purpose of present study is to demonstrate the effects of blend composition and shear on the phase inversion or phase formation in phase separated viscoelastic polymer blends. We found a coexisting structure ("walnut-like" scattering pattern) developed due to the shear-induced phase formation (SIPF) or phase inversion (SIPI) at a fixed composition and a constant temperature by light scattering and optical microscopy.

Experimental section

Materials: The polymers used in this study were supplied by Goodyear Tire and Rubber Company. The number-average relative molecular mass (M_n), the mass-average relative molecular mass (M_w), and the polydispersity of model polymers were determined by gel permeation chromatography (Waters Model 150-C). The microstructure of the model polymers was obtained by ^{13}C NMR. The results of the polymer characterization are summarized in Table 1.

Samples: The low-vinyl polybutadiene (LPB)/low-vinyl polyisoprene (LPI) and low-vinyl polybutadiene (LPB)/high-vinyl polyisoprene (HPI) blends used in this study were prepared by solution blending. All experiments were performed at a constant temperature, 130 °C, at which all the blends used in this study show phase-separated structures under quiescent conditions. The prepared LPB/LPI sample was heated from room temperature to 130 °C, then held for 120 min under quiescent conditions to obtain a reproducible two-phase morphology for each sample. In contrast, the prepared LPB/HPI sample was heated from room temperature to 130 °C, then held for 240 min under low shear rate ($\dot{\gamma}$ = 0.005 s^{-1}) to obtain a reproducible two-phase morphology for each sample.

Light scattering and optical microscopy: In-situ light scattering and optical microscopy instrument was designed and constructed for conducting the light scattering and optical microscope measurements under simple shear [6]. The phase separation temperature of the blend was determined by phase contrast optical microscopy (PCOM) [7].

Results and Discussion

Fig. 1 shows the two-dimensional SALS pattern and PCOM of the LPB/HPI blend A80 (ϕ_{HPI} = 0.8) at the various shear rates (0.005 s^{-1}, 0.05 s^{-1}, 1.0 s^{-1}, 10 s^{-1}, and 100 s^{-1}). The light scattering pattern shown in Fig. 1a is an isotropic at a shear rate 0.005 s^{-1}. Above 0.005 s^{-1} a streak again develops normal to the flow direction. The anisotropy of the streak is maximum at 1 s^{-1}, then decreases at higher shear rates. At 100 s^{-1}, we observed novel anisotropic scattering pattern such as "walnut-like pattern". It implies that there are two different periodic coexisting structures such as string-like domains and anisotropic domains (or butterfly-like pattern in Fourier space) with small characteristic length scales, ξ < 1 μm. Coexisting structure was developed by shear-induced phase formation (SIPF) or phase inversion (SIPI) in the blend A80. It implies that the matrix component of the HPI-rich phase may be converted to one of the coexisting phases under high shear.

The phase contrast optical micrographs of the structures corresponding to the SALS patterns are represented in Fig. 1b. The continuous and dispersed phases are HPI-rich and LPB-rich, respectively. At very low shear rate (0.005 s^{-1}), the domain structures are an isotropic and average droplet radius of LPB-rich domains is 3.4 ± 0.40 μm. With increasing shear rate, the LPB-rich domains elongate and break. A string-like pattern with extremely high aspect ratio (ζ > 25, ζ = L/W) appears at a shear rate 1 s^{-1}, where the L and W are the lengths of the domain in flow and vorticity directions, respectively. When the shear rate increases from 1 to 10 s^{-1}, the domain size in flow direction decreases. With a further increase in shear rate, 100 s^{-1}, the string-like structure almost disappears, and the micrograph shows new structure composed of the string-like and anisotropic domains in length scales (<1 μm). The detail structure is not shown clearly in the micrograps, but we clearly observed two different structures from the original image). This coexisting structure is responsible for the unique "walnut-like" SALS pattern in Fourier-space. The SALS pattern corresponding to $\dot{\gamma}$ = 100 s^{-1} represents the coexisting structures: LPB-rich string-like domains and HPI-rich anisotropic domains at the distribution of tilted angles to the flow direction. The anisotropic domains are responsible for the butterfly-like pattern in Fourier-space, and the butterfly-like pattern has also been observed in polymer gels and solutions [8]. We may infer from the coexisting SALS pattern that the dispersed domain represents the concentration enhancement ($\phi + \Delta\phi$) due to shear flow from the original concentration (ϕ) of HPI-rich domains under quiescent conditions, and the matrix represents the concentration decrease ($\phi - \Delta\phi$) in HPI-rich matrix. Thus the butterfly-like scattering pattern developed from the blend A80 can be explained by the coupling between concentration fluctuations and shear stress [9].

In order to confirm the coexisting structure observed from the LPB/HPI blend (A80), we carried out cessation of shear experiments [10]. Fig. 2 shows the SALS pattern from three different LPB/HPI blends: (a) A20 (ϕ_{HPI} = 0.2), (b) A40 (ϕ_{HPI} = 0.4), and (c) A80 (ϕ_{HPI} = 0.8). The number in the left upper corner of the SALS patterns represents shear rate in s^{-1}. For A20 and A40, the dispersed phase at the low shear rates such as 0.005 s^{-1} was HPI-rich component and isotropic. The HPI-rich domains with high viscosity represent the butterfly-like pattern at the high shear rates. For A20 and A40, the butterfly-like pattern disappeared after the shear was stopped. The relaxation times for A20 and A40 are 140 s and 120 s, respectively. In contrast, the relaxation time for the "walnut-like" pattern observed in A80 is relatively slow, and the pattern was not disappeared even until 1 hour after the shear was stopped. Therefore, we may conclude that the "walnut-like" scattering pattern corresponds to a coexisting structure of SIPF or SIPI in LPB/HPI blend, which converts very slowly back to the LPB-domain structure.

Table 1. Characterization Data of Polymers

sample code	M_n (g/mole)	M_w / M_n	η_0 (poise)*	vinyl content (%)
LPB	51000	1.03	2300	10
LPI	88000	1.08	6900	7
HPI	72000	1.02	19700	90

*Dynamic zero-shear viscosity was obtained at ω = 0.1 rad/s at 130 °C.

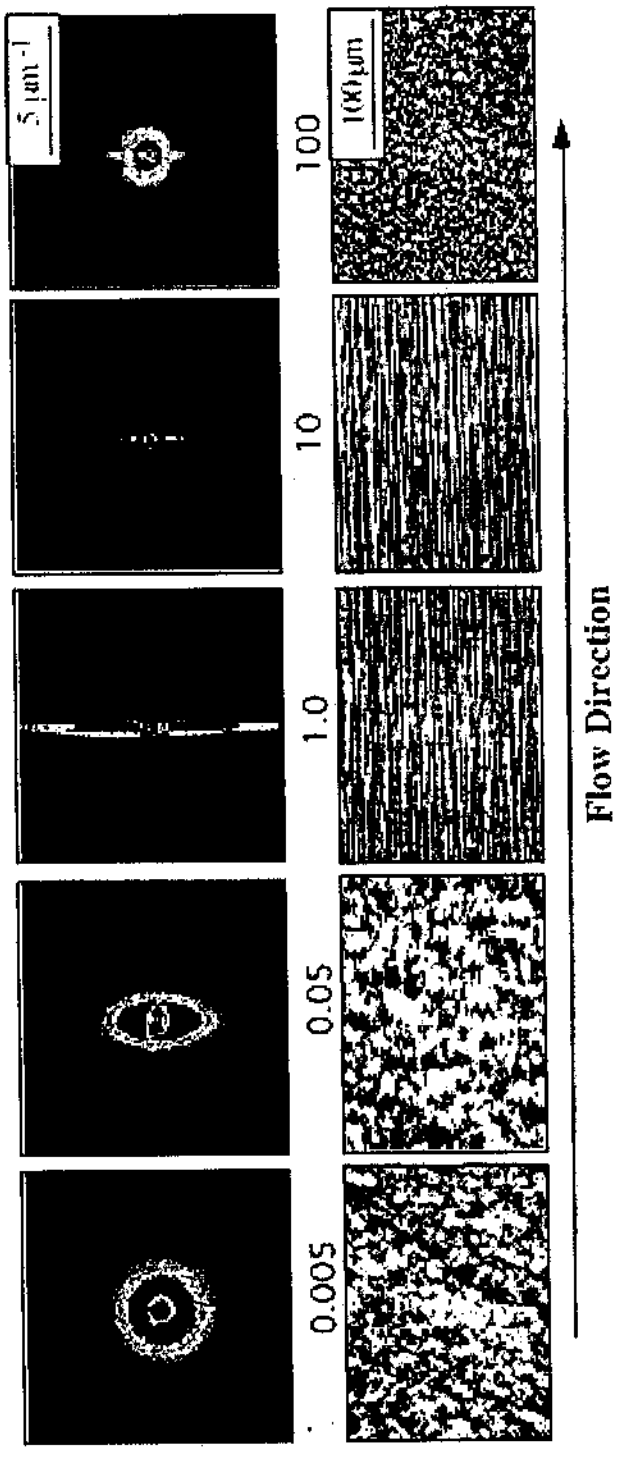

Figure 1. (a) Two-dimensional SALS patterns, (b) Optical micrographs of the LPB/HPI (A80) blend at different shear rates. The numbers under SALS patterns represent steady shear rate in s^{-1}.

Conclusions

We found a shear-induced coexisting structure responsible for the "walnut-like" scattering pattern in Fourier-space at a fixed composition by small angle light scattering (SALS) and phase contrast optical microscopy (PCOM). The coexisting structure is composed of two different periodic structures: string-like domain and anisotropic domain (butterfly-like pattern in Fourier-space) with small characteristic length scales, $\xi < 1$ μm. The cessation of shear experiment confirmed that the coexisting structure is developed by the shear-induced phase formation (SIPF) or phase inversion (SIPI).

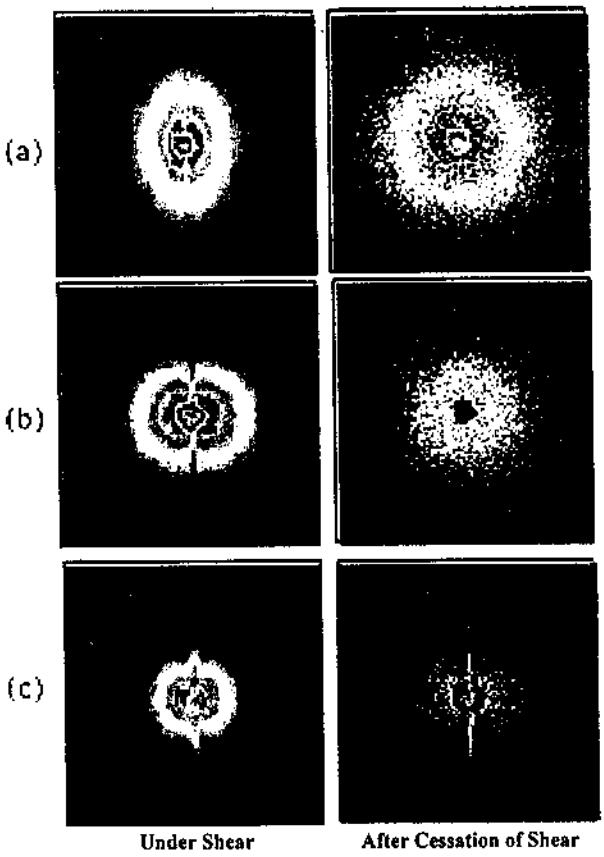

Figure 2. SALS patterns after cessation of shear from three different blends: (a) A20, (b) A40, and (c) A80. The numbers of SALS under shear flow represent steady shear rate in s^{-1}.

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References

1. Utracki, L.A. *Polymer Alloys and Blends*, Hanser Publishers, New York, 1990.
2. Han, C.D. *Rheology in Polymer Processing*, Academic Press, New York, 1976.
3. Paul, D.R.; Barlow, J. *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C18*, 109.
4. Jordhamo, G.M.; Manson, J.A.; Spering, L.H. *Polym. Eng. Sci.* **1986**, *26*, 517.
5. Miles, I.S.; Zurek, A. *Polym. Eng. Sci.* **1988**, *28*, 796.
6. Kim, S.; Yu, J. W.; Han, C. C. *Rev. Sci. Instrum.* **1996**, *67*, 3940.
7. Jeon, H. S.; Nakatani, A. I; Hsu, W.; Halasa, A. F.; Han, C. C. *ACS PMSE Preprint*, **1999**, *80*, 349.
8. Moses, E.; Kume, T.; Hashimoto, T. *Phys. Rev. Lett.* **1994**, *72*, 2037.
9. Helfand, E.; Fredrickson, G. H. *Phys. Rev. Lett.* **1989**, *62*, 2468.
10. Jeon, H.S.; Kim, S.; Han, C.C. submitted to *Macromolecules*.