Phase Inversion in Viscoelastic Polybutadiene (PB)/Polyisoprene (PI) Blends
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Introduction
Phase inversion in two-phase polymer blends is an important process for the control of morphology and properties in many practical areas, such as biomedical, cosmetic, food, membrane separation, and polymerization technologies [1-5]. 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 a phase inversion. Phase inversion in two-phase polymer blends is not as well understood as it is in emulsions. The morphology 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 determine the phase inversion composition from the morphology and rheological properties of phase-separated PB/PI blends obtained by a temperature quench from the single phase region into the two-phase region. We found that the phase inversion corresponds to discontinuities in the steady shear viscosity and dynamic storage modulus of binary PB/PI blends at high shear rate.

Experimental Section
The polymers used in this study were synthesized by living anionic polymerization. The number-average molecular weight (Mn) and the polydispersity of model polymers were determined by gel permeation chromatography. The microstructure of these materials was obtained by 1H NMR. The results of the polymer characterization are summarized in Table 1. For morphological and rheological experiments, the samples consisting of PB and PI with mass fractions of PI ranging from 0.1 to 0.9 were prepared by solution blending [6]. Thin samples (ca. 0.43 mm in thickness and 23 mm in outer diameter) were used for both morphology and cloud point measurements. The quiescent phase transition temperature of the blend was determined by phase contrast optical microscopy using a step heating method [7]. The morphology under simple shear flow was measured with an in-situ shear light scattering/microscope instrument [8].

A Rheometric Scientific SR-500 controlled stress rheometer was utilized in the parallel plates geometry with adjustable sample thickness [9]. Our measurements were carried out with 25 mm diameter fixtures and a sample gap of 0.4±0.01 mm. The temperature was controlled by electrically heated top and bottom plates with an accuracy ±0.1 °C This blend exhibits lower critical solution temperature (LCST) type phase behavior. Here, the blend is single phase at low temperatures and phase separated at elevated temperatures. The prepared sample was heated from room temperature to 130 °C, then held for 120 min to obtain a reproducible two-phase morphology for each sample. Thus, we do not need a preshear before we start the measurements. Oscillatory shear measurements were carried out on small strain, 8%, over the full concentration range from 0.1 to 1.0 mass fraction PI in the frequency range between 0.1 to 100 rad/s. Steady shear measurements were also carried out on the identical PB/PI blends used in the oscillatory shear measurements over the shear rates range from 0.001 s⁻¹ to 10 s⁻¹. The measurements were carried out under N₂ atmosphere to prevent degradation at the experimental temperature, 130 °C.

Results and Discussion
Fig. 1 shows the phase diagram of the PB/PI mixture, and the average radius of the dispersed phase as a function of PI-concentration (ΦPI). The average droplet radius of dispersed phase under quiescent conditions was obtained after being held for 120 min at 130°C [10]. The lower critical solution temperature was 62 ± 1.0 °C at the critical composition, ΦPI = 0.45 ± 0.05. The droplet size increases between the volume fraction values of PI 0.1 to 0.6, while a decrease in droplet size is observed from the volume fraction values of 0.6 to 0.8. A maximum in the droplet radius with a change of composition is observed at ΦPI = 0.60 ± 0.05.

In Fig. 2, we show the steady shear viscosity versus ΦPI at two selected shear rates of 0.001 s⁻¹ and 0.1 s⁻¹. The domain deformation at these shear rates is shown in Fig. 3. The low shear rate (S = 0.001 s⁻¹) does not alter the droplet shape of the dispersed phase in our blends. At the low shear rate, we observed a continuous increase of the blend viscosity as the volume fraction increases from 0.1 to 0.6. In contrast, the blend viscosity decreases systematically for ΦPI > 0.6, indicating that the dispersed phase may be inverted from PI-rich to PB-rich. This behavior may be explained qualitatively using a theory for the mixtures of two Newtonian liquids developed by Choi & Schowalter [11]. The resulting equation for the viscosity of the concentrated emulsions is given by:

$$\eta = \eta_m \left[ 1 + \phi \left( \frac{2 + 5\lambda}{2} \right) + \phi^2 \left( \frac{2 + 5\lambda}{2} \right)^2 \right]$$  

(1)

where $\lambda$ is the viscosity ratio, $\eta_m$ is the viscosity of dispersed phase, $\eta_m$ is the viscosity of matrix phase, and $\eta_0$ is the viscosity of the dispersed phases, respectively. The equation was derived for the emulsion system with a monodisperse particle size distribution. The emulsion viscosity at a fixed value of $\phi$ is only a function of $\lambda$. The viscosity has a minimum and is equal to the viscosity of matrix phase if the volume fraction is set to zero, and a continuous increase of $\eta$ in $n_1$ (1) is evident until the volume fraction reaches a maximum value. In this case, we are looking at a two-phase blend, it is not exactly the same as emulsions. If we start from either pure PI or PB sides of the phase diagram, and neglect the viscosity change of the matrix component, then the maximum viscosity is limited to the phase interfacial area [14], which has a minimum value for completely elongated droplets. Since our phase separated polymer blend is directly related to the phase morphology, the shear viscosity of phase separated blends is generally given as, $\eta = \eta_0 + \Delta\eta$, where $\eta_n$ is the viscosity of the blend in single phase state and $\Delta\eta$ is an excess shear viscosity due to the domain interface of phase separated blends. It is well known that $\Delta\eta$ arises from excess shear stress due to domain interfaces, in which excess shear stress was given by [12-14]

$$\Delta\eta = \nabla \cdot \nabla \frac{P}{\gamma}$$

(2)

where $\nabla = (n_{xx}, n_{yy}, n_{zz})$ is the unit normal vector of domain interfaces, $\sigma$ is the surface tension, $\nu$ is the volume of the system, $da$ is the surface element along the interface, and the integral is performed over the surfaces of domain interfaces. We observed a systematic increase of the viscosity in the PB-rich matrix phase for $\Phi PI < 0.55$ or the PI-rich matrix phase for $\Phi PI > 0.55$ at S = 0.1 s⁻¹ in Fig. 2. This observation can be easily explained by eq. (2). It is because the excess shear viscosity is proportional to the phase interfacial area [14], which has a minimum value for completely elongated domains. Since our phase separated critical PB/PI blend at S = 0.1 s⁻¹ forms string-shaped domains, this has a small contribution to the effective shear viscosity. As the $\Phi PI$ increases further, a discontinuity of $\eta$ at $\Phi PI = 0.55$ is evident, which indicates that the continuous phase is inverted from PB-rich matrix to PI-rich matrix. Thus, at the high shear rate, the phase inversion composition from PI-rich domains to PB-rich domains is $\Phi PI = 0.55 ± 0.05$.

In Fig. 4 we show the dynamic storage modulus, G', versus $\Phi PI$ for the selected frequencies of 0.1 rad/s and 10 rad/s. The compositional dependence of the storage modulus at higher frequency 10 rad/s shows a discontinuity at $\Phi PI = 0.55$. It is interesting to note that this corresponds to the phase inversion composition obtained from the discontinuities of steady shear viscosity at high shear rate as a function of composition. In general, G' increases with the increase in the volume fraction of PI at high frequencies to be estimated by means of a linear mixing rule (4, 15). Again the break in G' can be interpreted as a discontinuity in phase morphology or phase inversion. At a low frequency $\omega = 0.1$ rad/s, a systematic increase of G' until $\Phi PI = 0.6$ is evident, indicative of the increases in the concentration and size of the PI-rich droplets in the PB-rich continuous phase. Again similar to the case of the viscosity at low shear rate, for $\Phi PI > 0.6$ the blend modulus decreases continuously, indicating that dispersed phase is inverted from PI-rich domains to PB-rich domains. The strong compositional dependence of G' at this low frequency may come from the perturbation of the domain shape under oscillatory shear, which in turn is related to the domain size [15, 16].
Conclusions
We determined the phase inversion compositions in PB/PI blends based on the discontinuity of steady-shear viscosity and dynamic storage modulus at low and high shear rates. The domains were elongated at high shear rate (0.1 s⁻¹), while not elongated at low shear rate (0.001 s⁻¹). The phase inversion composition in our blend is affected by low and high shear rates. At the high shear rate, we found a discontinuity in the steady shear viscosity and dynamic storage modulus at $\phi_{pl, i} = 0.55 \pm 0.05$, while at the low shear rate (or quiescent condition) the observed $\phi_{pl, i} = 0.6 \pm 0.05$. These values can be compared with the predicted value of 0.61 [17].

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References
9. Certain commercial equipment, instruments, or materials are identified in this article in order to specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
10. The average radius of dispersed phase was obtained by examining a full micrograph (200 μm x 160 μm) and averaging 25 to 65 droplets per sample.

Table 1. Characterization Data

<table>
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<tr>
<th>sample code</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w / M_n$</th>
<th>$\eta_0 \times 10^{-3}$ (poise)</th>
<th>microstructure, mole %</th>
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<td>2.31</td>
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<tr>
<td>PI</td>
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<td>1.08</td>
<td>6.90</td>
<td>90, 10</td>
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</tbody>
</table>

Flow direction

Figure 1. Phase diagram of PB/PI blends, and compositional dependence of the average droplet radius of phase separated PB/PI blends at 130 °C.

Figure 2. The compositional dependence of the steady shear viscosity of PB/PI blends at the selected shear rates (0.001 s⁻¹ and 0.1 s⁻¹) at 130 °C.

Figure 3. The scattering patterns and optical micrographs of critical PB/PI (60/40) blend under simple shear flow at 130 °C (a) isotropic at $S = 0.001$ s⁻¹ and (b) anisotropic at $S = 0.1$ s⁻¹.

Figure 4. The compositional dependence of the storage modulus of PB/PI blends at the selected frequencies ($\omega=0.1$ rad/s and $\omega=10$ rad/s) at 130 °C.