

Effects of Domain Interfaces on the Rheological Properties of Polybutadiene/Polyisoprene Blends

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Introduction

The rheology and morphology of viscoelastic polymer blends are of great research interest to both academic and industrial communities since they are essential factors in various heterogeneous polymer systems. Viscoelastic polymer blends such as polybutadiene (PB)/polyisoprene (PI) can be homogeneous or heterogeneous depending upon industrial processing conditions. Rheological properties of multiphase systems are strongly influenced by the morphology, which depends on the thermodynamic interactions between the two constituent polymers. [1, 2].

We investigated the viscoelastic properties of entangled PB/PI blends above and below the lower critical solution temperature (LCST) by oscillatory shear rheology. The phase separated PB/PI blends, within the linear viscoelastic regime, display high values of the storage modulus at low frequencies. This is due to the interfacial tension between the two phases of the blends. In contrast, the loss modulus of the blends at low and high frequencies is not affected by the interfacial tension. In order to study the effects of interfacial tension on the dynamic moduli, we calculated G' and G'' with Gramespacher and Meissner's model equation [3] derived from a theory for mixtures of Newtonian liquids developed by Choi and Schowalter [4]. In the phase separated state, the theoretical prediction revealed that the large values of the storage modulus at low frequencies depend directly on the interfacial tension as well as the size and shape of the dispersed domains.

We found a discontinuity in the temperature dependence of viscoelastic properties such as the storage modulus, the loss modulus, and the dynamic viscosity. The discontinuity is related to the phase separation temperature of the PB/PI blends, while the rheologically determined phase separation temperature at various frequencies was much higher than that obtained from phase contrast optical microscopy [5]. The discontinuity measured from G' corresponds to the macro-phase separation temperature (T_C), and T_C strongly depends on the frequency, ω .

Experimental section

The polymers used in this study were supplied by Goodyear Tire and Rubber Company. The polybutadiene and polyisoprene chains are statistical copolymers, composed of 1-4, 1-2 isomers and 1-4, 3-4 isomers, respectively. The zero-shear viscosity was obtained at $\omega = 0.1$ rad/s. The results of the polymer characterization are summarized in Table 1. The phase separation temperature of the blend was determined by phase contrast optical microscopy [6]. A near critical PB/PI blend, labeled as D40, has a lower critical solution temperature (LCST) of 62 ± 1 °C, hence, the blend is a single phase at low temperatures (< 62 °C) and phase separated at elevated temperatures (> 62 °C).

A Rheometric Scientific SR-5000 rheometer was utilized in the parallel-plate geometry for oscillatory shear measurements. Our measurements were carried out with 25 mm diameter fixtures and $0.4 \text{ mm} \pm 0.01 \text{ mm}$ gap thickness. The temperature was controlled by electrically heated top and bottom plates to within ± 0.1 °C. The measurements were carried out under nitrogen atmosphere to prevent any thermal degradation of the polymers which are known to be extremely sensitive to heat. In order to study the linear viscoelastic properties at low frequencies, the oscillatory shear measurements were performed in a constant strain mode with a small strain amplitude ($\gamma_0 = 0.08$).

Results and Discussion

Fig. 1 shows the storage and loss moduli for the homopolymers (PB and PI) and a near critical PB/PI blend D40 ($\phi_{PB}/\phi_{PI} = 3/2$) at 130 °C. At high frequencies ($\omega > 10^6$ rad/s), the values of the storage modulus for the blend lie between the storage moduli of the homopolymers. However, at low

frequencies ($< 10^6$ rad/s), the storage modulus of the blend shows a large deviation from the log additive mixing rule. The deviation is characterized by an emergence of a pronounced storage modulus at low frequencies, which is presumed to be due to the interfacial tension. This implies that the dispersed domains are behaving purely elastically even though they are made of viscoelastic materials. In contrast, the loss modulus of the blend lies between the loss modulus values for the homopolymers over the entire frequency range. The intermediate modulus values for the blend are consistent with a log-additive mixing rule [2]. The log-additive mixing rule is given by,

$$\log G = \phi_{PB} \log G_{PB} + \phi_{PI} \log G_{PI} \quad (1)$$

where G is the storage or loss modulus of the binary blend and G_j is the storage or loss modulus of each component j .

For the description of the influence of the interfacial tension on the moduli we use Gramespacher and Meissner's results [3] derived from a theory for mixtures of Newtonian liquids developed by Choi and Schowalter [4]. The results are given by equations 2 and 3:

$$G'_{\text{blend}} = G'_{\text{components}} + G'_{\text{interface}} \\ = (\phi_A G'_A + \phi_B G'_B) + \frac{\eta}{\tau_A} \left(1 - \frac{\tau_B}{\tau_A} \right) \frac{\omega^2 \tau_A^2}{1 + \omega^2 \tau_A^2} \quad (2)$$

$$G''_{\text{blend}} = G''_{\text{components}} + G''_{\text{interface}} \\ = (\phi_A G''_A + \phi_B G''_B) + \frac{\eta}{\tau_A} \left(1 - \frac{\tau_B}{\tau_A} \right) \frac{\omega \tau_A}{1 + \omega^2 \tau_A^2} \quad (3)$$

where

$$\eta = \eta_m \left[1 + \phi_A \frac{5(\lambda + 2)}{2(\lambda + 1)} + \phi_A^2 \frac{5(5\lambda + 2)}{8(\lambda + 1)^2} \right] \quad (4)$$

$$\tau_A = \tau_0 \left[1 + \phi_A \frac{5(19\lambda + 16)}{4(\lambda + 1)(2\lambda + 3)} \right] \quad (5)$$

$$\tau_B = \tau_0 \left[1 + \phi_A \frac{3(19\lambda + 16)}{4(\lambda + 1)(2\lambda + 3)} \right] \quad (6)$$

$$\tau_0 = \frac{\eta_m R (19\lambda + 16)(2\lambda + 3)}{\sigma 40(\lambda + 1)} \quad (7)$$

$$\lambda = \frac{\eta_d}{\eta_m} \quad (8)$$

In these equations η_d and η_m are the Newtonian viscosity of the dispersed phase and matrix of the mixture, respectively, λ is the viscosity ratio, R is the radius of the monodisperse droplets, and σ is the interfacial tension. For the application of these equations to our PB/PI blends, the following assumptions were made: (1) The viscosity of the PB-rich matrix phase is equal to the viscosity of the pure PB component, and the viscosity of the PI-rich dispersed phase is equal to the viscosity of the pure PI component, (2) The radius of dispersed droplets in the blends is almost monodisperse.

Fig. 2 shows the effect of interfacial tension on the calculated dynamic moduli (G' and G'') of the blend D40 for a given value of the volume fraction ($\phi_{PI} = 0.4$) and average radius ($R = 11.5 \mu\text{m}$) of the dispersed droplets based on equations 2 and 3. Since the volume fraction, droplet radius, and viscosity are all known, the only adjustable parameter for the results shown in Fig. 2 is the interfacial tension, σ . The average radius of the dispersed droplets of the blend was obtained from the optical microscopy measurement [5]. The curves calculated from the equations 2 and 3 as a function of interfacial tension

represent the effect of domain interfaces on G' and G'' . At high frequencies ($\omega > 10$ rad/s), it is evident that the storage modulus is not affected by the interfacial tension, whereas the storage modulus at lower frequencies ($\omega < 10$ rad/s) is sensitive to the interfacial tension value, which implies that the high values of G' at low frequencies are due to the interfaces in the blend. In contrast, the loss modulus of the blend is not affected by the interfacial tension and identical with the predictions from the matrix and dispersed components. Therefore, it is clear that the high values of G' at low frequencies can be explained quantitatively by the contribution of the interfacial tension of the phase separated blend from equation 2. For a fixed volume fraction, if the interfacial tension increases or the droplet size decreases, the pronounced elasticity at low frequencies increases according to the predictions of the model equation.

Fig. 3 shows the dependencies of G' on temperature at different frequencies ($\omega = 0.1$ rad/s, $\omega = 0.4$ rad/s, $\omega = 1.0$ rad/s, $\omega = 2.5$ rad/s, $\omega = 5.0$ rad/s, and $\omega = 10$ rad/s) for D40. It is clear that there are discontinuities in the slopes of $\log G'$ vs. T^{-1} at different temperatures as a function of frequency. The discontinuity of G' is strongly dependent on the frequency of the oscillatory shear measurements. In the homogeneous regime, an increase in temperature results in a decrease of G' due to the increase of chain mobility. The homogeneous mixture has WLF dependence on temperature, which is typical for the most single-phase polymer systems in the terminal viscoelastic regime. As the temperature increases further into the two-phase region, however, the storage modulus at low frequencies ($\omega < 10$ rad/s) is dominated by the interfacial tension between the droplets and the matrix [3], and the interfacial tension has only a weak temperature dependence. Using the above information, we assign the point of change in the slope of $\log G'$ vs. T^{-1} plot to the phase separation temperature (T_c) indicated by arrows.

Table 1. Characterization Data of Polymers

sample code	M_n (g/mole)	M_w / M_n	η_0 (poise) at 130 °C	microstructure, mole %		
				1, 4	1, 2	3, 4
PB	51000	1.03	2300	90	10	-
PI	88000	1.08	6900	93	-	7

Conclusions

In the effect of domain size and interface, we found that the phase separated PB/PI blends, within the linear viscoelastic regime, display high values of storage modulus at low frequencies. This is due to the interfacial tension between the two phases of the blend. In contrast, the loss modulus of the blends at low and high frequencies is not affected by the interfacial tension.

We found a discontinuity in the temperature dependence of the dynamic storage modulus in the rheological determination of macrophase separation temperature. The discontinuity is related to T_c of the PB/PI blend, and is a function of the oscillatory frequency. Therefore, we suggest that the frequency effect on T_c should be carefully considered when determining T_c by oscillatory shear measurements.

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References

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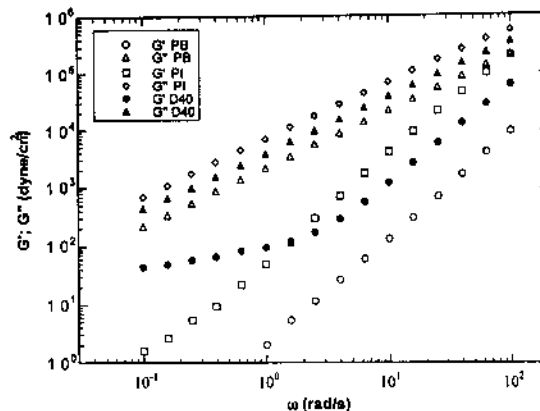


Figure 1. Dynamic storage modulus (G') as a function of frequency for PB (open circles), PI (open squares), D40 (closed circles) and dynamic loss modulus (G'') for PB (open triangles), PI (open diamonds), D40 (closed triangles) at 130 °C.

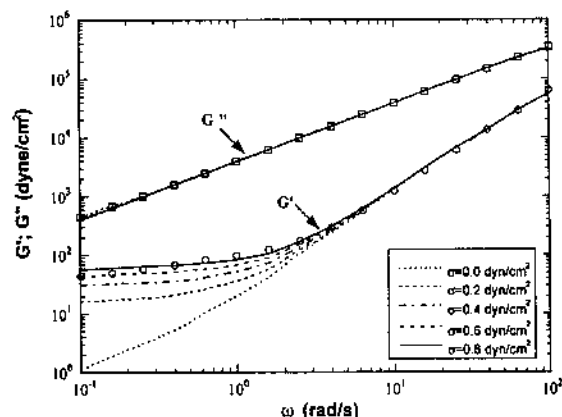


Figure 2. The effect of interfacial tension on the calculated dynamic storage and loss moduli of D40 for a given value of the volume fraction ($\phi_{PI} = 0.4$) and average radius ($R = 11.5 \mu\text{m}$) of the dispersed droplets based on equations 2 and 3. Measured storage (open circle) and loss (open square) moduli for D40 at 130 °C. The droplet radius of dispersed phase used in the calculation of G' and G'' was independently measured under quiescent conditions by using optical microscopy.

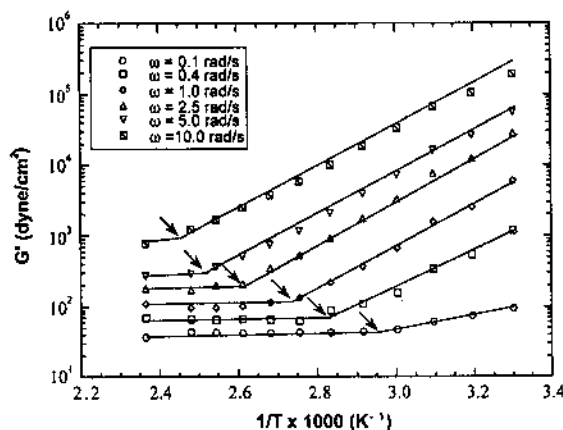


Figure 3. The dependencies of G' on temperature at different frequencies ($\omega = 0.1$ rad/s, $\omega = 0.4$ rad/s, $\omega = 1.0$ rad/s, $\omega = 2.5$ rad/s, $\omega = 5.0$ rad/s, and $\omega = 10$ rad/s) for a near critical PB/PI blend (D40). The arrows indicate the phase separation temperature of the blend D40 at each frequency.