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Description	

## Effects of Droplet Size and Volume Fraction on Relaxation Modulus of Immiscible Polymer Blends: Inclusion of Interface Velocity Term

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Stress relaxation behavior was investigated under large step shear strains  $\gamma$  for polyisobutylene/poly(dimethyl siloxane) blends with different average droplet-size. The interfacial contribution to the relaxation modulus,  $G_{\text{int}}(t, \gamma)$ , was evaluated by subtraction of the matrix contribution from the relaxation modulus of the blend, assuming the linear additivity rule for the relaxation modulus. The interfacial modulus  $G_{\text{int}}(t, \gamma)$  for the blends with different average droplet-size obtained at the same strain can be superposed in a reduced form,  $G_{\text{int}}(t, \gamma)/(\Gamma\phi/r_v)$  vs.  $t/\tau_D$ , where  $\Gamma$  is the interfacial tension,  $\phi$  the volume fraction of the droplet phase,  $r_v$  the volume-averaged radius of droplets, and  $\tau_D$  is the linear viscoelastic relaxation time of the droplets (interface). Superposition can be applied for the blends with  $\phi = 0.108$  and  $0.214$ . The superposition is developed from consideration on the theoretical expression for the stress tensor which includes both contributions from the interface velocity term and Laplace pressure term. It is suggested from the good superposition that contribution from droplet-droplet interactions to the stress can be neglected in the present blends with  $\phi \leq 0.214$  or that the contribution is also reduced by the same factors as  $(\Gamma\phi/r_v)$  and  $t/\tau_D$ .

**Key Words:** Stress relaxation / Polymer blend / Droplet size / Relaxation time / Interface velocity

### 1. INTRODUCTION

It is an essential subject in rheology of immiscible polymer blends to clarify the effects of droplet size and volume fraction of droplet phase on the rheological properties of the blends. In linear viscoelasticity, the theory developed by Palierne<sup>1)</sup> well describes the effects of droplet size and volume fraction.<sup>2)</sup> In this theory, the plateau modulus  $G_D$  and the relaxation time  $\tau_D$  due to deformation and recovery of droplets are respectively given by<sup>1,2)</sup>

$$G_D = 20 \frac{\Gamma\phi}{r_v} \frac{1}{(2K + 3 - 2\phi(K - 1))^2}, \quad (1)$$

$$\tau_D = \frac{r_v\eta_m}{4\Gamma} \frac{(19K + 16)(2K + 3 - 2\phi(K - 1))}{10(K + 1) - 2\phi(5K + 2)}, \quad (2)$$

where  $\Gamma$  represents the interfacial tension between the droplet phase and the matrix phase and  $\phi$  the volume fraction of the

droplet phase.  $r_v$  is the volume-averaged radius of droplets and is defined by

$$r_v = \frac{\sum_{i=1}^N \phi_i r_i}{\sum_{i=1}^N \phi_i}$$

where  $r_i$  denotes the radius of  $i$ -th droplet,  $\phi_i$  the volume fraction of  $i$ -th droplet and  $N$  the total number of the droplets.  $K$  represents the viscosity ratio and is defined by  $\eta_d/\eta_m$  where  $\eta_m$  and  $\eta_d$  denote the zero shear viscosity of the matrix and the droplets, respectively. In Eqs. (1) and (2), the effect of  $r_v$  and  $\phi$  on  $G_D$  and  $\tau_D$  is clear.

On the other hand, under large deformation, effects of droplet size and volume fraction on rheological behaviors of polymer blends are not yet clearly understood. Yamane et al.<sup>3)</sup> observed shape recovery of an isolated polyisobutylene (PIB) droplet in poly(dimethyl siloxane) (PDMS) matrix. They found that increase in the shear strain  $\gamma$  delays the recovery of the droplet. Hayashi et al.<sup>4)</sup> performed the same experiments using PIB droplets with different radii and found that time evolution of droplet shape can be reduced by  $\tau_D$  at each  $\gamma$  even

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for large  $\gamma$  where the time evolution exhibits significant delay. Concerning the stress relaxation under large step shear strains, it has been shown that the stress tensor representing the contribution from pressure difference beyond the interface (the Laplace pressure term), which corresponds to the stress tensor calculated by the interface tensor<sup>5,6)</sup>, is reduced by  $\Gamma\phi/r_0$  for a single droplet, where  $r_0$  is the droplet radius before deformation.<sup>7,8)</sup> Comparison of this theoretical prediction with the experimental results indicates that  $\Gamma\phi/r_0$  roughly reduce the stress relaxation modulus of blends.<sup>7,8)</sup> In this comparison, the time scale is assumed to be reduced by the linear relaxation time  $\tau_D$  similarly to the shape recovery of isolated droplets. The comparison shows that  $\tau_D$  roughly reduce the time scale also at large strains. Though these results indicate that  $\Gamma\phi/r_0$  and  $\tau_D$  are respectively good scales for the relaxation modulus and time, further systematic investigations are clearly necessary. In addition, another source of stress, i.e., contribution from viscous flow of components caused by motion of the interface (the interface velocity term) should be considered. The interface velocity term may have significant influence on the stress tensor if viscosities of components are different.<sup>9-14)</sup> Actually, in the last stage of stress relaxation under large step shear strains, the interface velocity term is 37 % of the Laplace pressure term at the beginning and 50 % at the end, which are evaluated using a theoretical model for retraction of a spheroidal droplet with  $K = 0.081$  and supported by experimental results of stress relaxation for a PIB/PDMS blend.<sup>14)</sup> Until now it is not known how relaxation modulus and time for blends with different droplet size and volume fraction are respectively reduced when the contribution of the interface velocity term is included.

The objective of the present study is to find the effects of droplet size and volume fraction of droplets on stress relaxation under large step shear strains with consideration of both interface velocity term and Laplace pressure term. Stress relaxation under large step shear strains is a useful method to investigate the behavior under large deformation since large step deformation is instantaneously applied to droplets and then stress relaxation due to the interfacial tension can be observed under no external flow. The experimental results of the stress relaxation are discussed based on the theoretical expression for the stress tensor due to the interface<sup>9,10)</sup>, which includes contributions from the Laplace pressure and the interface velocity, and the applicability of the theoretical expression is examined.

## 2. THEORETICAL BACKGROUND

### 2.1 Stress Relaxation of an Isolated Droplet

Let us consider an isolated ellipsoidal droplet with semi-axes  $a$ ,  $b$  and  $c$  ( $a \geq c \geq b$ ) in a matrix with infinitely large volume. The radius of the droplet before deformation is  $r_0$ . The droplet and the matrix phases are assumed to be Newtonian fluids. Stress tensor  $\boldsymbol{\sigma}$  for mixtures of two Newtonian fluids can be written as<sup>9,10)</sup>

$$\boldsymbol{\sigma} = -p\boldsymbol{\delta} + \eta_m[\nabla\mathbf{v} + (\nabla\mathbf{v})^T] - \frac{(\eta_m - \eta_d)}{V} \int_{S_0} dS(\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u}) + \frac{\Gamma}{V} \int_{S_0} dS\left(\frac{1}{3}\boldsymbol{\delta} - \mathbf{n}\mathbf{n}\right), \quad (3)$$

where  $p$  is the isotropic part of the stress,  $\boldsymbol{\delta}$  the unit tensor,  $\nabla\mathbf{v}$  the velocity gradient tensor,  $V$  the total volume of the system,  $S_0$  the total area of the interface,  $\mathbf{u}$  the local velocity vector,  $\mathbf{n}$  the unit outward normal vector on the interface. The Reynolds number is assumed to be so small that we can neglect inertial force. The first term in Eq. (3) represents the isotropic pressure. The second term expresses the viscous stress of the matrix fluid without any dispersed phase. The third term represents the contribution from the viscous flows of the matrix phase and the dispersed phase due to the local flow caused by the displacement of the interface. The fourth term arises from the difference of the normal stress beyond the interface due to the Laplace pressure.<sup>9,15)</sup> In the present study, we denote the third and the fourth terms as the interface velocity term  $\boldsymbol{\sigma}_v$  and the Laplace pressure term  $\boldsymbol{\sigma}_L$ .

The interface velocity term  $\boldsymbol{\sigma}_v$  can be rewritten as

$$\begin{aligned} \boldsymbol{\sigma}_v &= -\frac{(\eta_m - \eta_d)}{V} \int_{S_0} dS(\mathbf{u}\mathbf{n} + \mathbf{n}\mathbf{u}) \\ &= -\frac{(\eta_m - \eta_d)}{V} \int_{V_0} dV(\nabla\mathbf{u} + (\nabla\mathbf{u})^T). \end{aligned} \quad (4)$$

While the flow field around the droplet is complex, the instantaneous local velocity  $\mathbf{u}$  in the droplet including the interface can be written as<sup>11,14,16)</sup>

$$\mathbf{u} = (\mathbf{R} \cdot \mathbf{L} \cdot \mathbf{R}^T) \cdot \mathbf{x}. \quad (5)$$

In Eq. (5),  $\mathbf{L}$  is a droplet velocity gradient tensor defined as a function of time  $t$  and strain  $\gamma$  in Cartesian coordinates  $\mathbf{X} = (X, Y, Z)$ ,

$$\mathbf{L}(t, \gamma) = \begin{pmatrix} \partial \ln(a/r_0)/\partial t & 0 & 0 \\ 0 & \partial \ln(b/r_0)/\partial t & 0 \\ 0 & 0 & \partial \ln(c/r_0)/\partial t \end{pmatrix}, \quad (6)$$

where  $X$ ,  $Y$  and  $Z$  axes are parallel to the semi-axes of the ellipsoidal droplet,  $a$ ,  $b$  and  $c$ , respectively. The coordinates

$\mathbf{x} = (x, y, z)$  in Eq. (5) represent Cartesian coordinates of the experimental frame, where  $x$ ,  $y$  and  $z$  correspond to directions of flow, velocity gradient and vorticity, respectively, and  $\mathbf{R}$  the tensor of the transformation from  $\mathbf{X}$  to  $\mathbf{x}$ .

The direct observations of the recovery of droplets under large step shear strains show that orientation angle  $\theta$ , which is defined by the angle between the semi-axis  $a$  and the coordinate  $x$ , is independent of time and coincides with the angle given by the affine deformation assumption for droplets with  $0.048 \leq K \leq 0.54$ .<sup>3,17,18)</sup> This means that  $\mathbf{R}$  is independent of time and that  $\theta$  is given by

$$2 \cot 2\theta = \gamma. \quad (7)$$

Another experimental results indicate that  $a/r_0$ ,  $b/r_0$  and  $c/r_0$  are given by functions of  $t/\tau_D$  and  $\gamma$ , which are independent of  $r_0$ .<sup>4)</sup> Based on the results, we define reduced droplet velocity gradient tensor  $\mathbf{\Lambda}$  as a function of  $t/\tau_D$  and  $\gamma$  by

$$\mathbf{\Lambda}(t/\tau_D, \gamma) = \begin{pmatrix} \partial \ln(a/r_0)/\partial(t/\tau_D) & 0 & 0 \\ 0 & \partial \ln(b/r_0)/\partial(t/\tau_D) & 0 \\ 0 & 0 & \partial \ln(c/r_0)/\partial(t/\tau_D) \end{pmatrix}. \quad (8)$$

Equations (6) and (8) lead to

$$\mathbf{L}(t, \gamma) = \mathbf{\Lambda}(t/\tau_D, \gamma)/\tau_D. \quad (9)$$

Substituting Eqs. (2), (5) and (9) into Eq. (4) yields

$$\begin{aligned} \sigma_v(t, \gamma) = & -\frac{\Gamma\phi}{r_0} \frac{40(K+1)(1-K)}{(19K+16)(2K+3)} \\ & \mathbf{R} \cdot (\mathbf{\Lambda}(t/\tau_D, \gamma) + \mathbf{\Lambda}^T(t/\tau_D, \gamma)) \cdot \mathbf{R}^T, \end{aligned} \quad (10)$$

where  $\phi$  for the isolated droplet is assumed to be  $\phi \ll 1$ . Then the interface velocity term of the shear stress,  $\sigma_{v,xy}(t, \gamma)$ , is given by

$$\begin{aligned} \sigma_{v,xy}(t, \gamma) = & -\frac{\Gamma\phi}{r_0} \frac{40(K+1)(1-K)}{(19K+16)(2K+3)} \\ & \sin 2\theta (\Lambda_{xx}(t/\tau_D, \gamma) - \Lambda_{yy}(t/\tau_D, \gamma)). \end{aligned} \quad (11)$$

Since  $\theta$  is a function of  $\gamma$  as shown in Eq. (7), Eq. (11) can be rewritten as

$$\sigma_{v,xy}(t, \gamma) = \frac{\Gamma\phi}{r_0} \sigma_{v,xy}^0(t/\tau_D, \gamma), \quad (12)$$

with

$$\begin{aligned} \sigma_{v,xy}^0(t/\tau_D, \gamma) = & -\frac{40(K+1)(1-K)}{(19K+16)(2K+3)} \\ & \sin 2\theta (\Lambda_{xx}(t/\tau_D, \gamma) - \Lambda_{yy}(t/\tau_D, \gamma)) \end{aligned}$$

where  $\sigma_{v,xy}^0(t/\tau_D, \gamma)$  is a reduced shear stress for the interface

velocity term.

Concerning the Laplace pressure term  $\sigma_L$ , shear component  $\sigma_{L,xy}$  for the ellipsoidal droplet can be written as<sup>7,8)</sup>

$$\begin{aligned} \sigma_{L,xy} = & -\left(\frac{3\Gamma\phi}{8\pi r_0}\right) \sin 2\theta \int_0^{2\pi} d\Phi \int_0^\pi d\Theta \sin \Theta \\ & \frac{\cos^2 \Theta}{(a/r_0)^2} - \frac{\sin^2 \Theta \cos^2 \Phi}{(b/r_0)^2} \\ & \sqrt{\frac{\cos^2 \Theta}{(a/r_0)^2} + \frac{\sin^2 \Theta \cos^2 \Phi}{(b/r_0)^2} + \frac{\sin^2 \Theta \sin^2 \Phi}{(c/r_0)^2}}, \end{aligned} \quad (13)$$

where  $\Theta$  and  $\Phi$  are parameters to describe ellipsoid. Since  $a/r_0$ ,  $b/r_0$  and  $c/r_0$  are functions of  $t/\tau_D$  and  $\gamma$  and  $\theta$  is a function of  $\gamma$  as shown in Eq. (7),  $\sigma_{L,xy}$  can be rewritten as

$$\sigma_{L,xy}(t, \gamma) = \frac{\Gamma\phi}{r_0} \sigma_{L,xy}^0(t/\tau_D, \gamma). \quad (14)$$

with

$$\begin{aligned} \sigma_{L,xy}^0(t/\tau_D, \gamma) = & -\left(\frac{3}{8\pi}\right) \sin 2\theta \int_0^{2\pi} d\Phi \int_0^\pi d\Theta \sin \Theta \\ & \frac{\cos^2 \Theta}{(a/r_0)^2} - \frac{\sin^2 \Theta \cos^2 \Phi}{(b/r_0)^2} \\ & \sqrt{\frac{\cos^2 \Theta}{(a/r_0)^2} + \frac{\sin^2 \Theta \cos^2 \Phi}{(b/r_0)^2} + \frac{\sin^2 \Theta \sin^2 \Phi}{(c/r_0)^2}} \end{aligned}$$

where  $\sigma_{L,xy}^0(t/\tau_D, \gamma)$  is a reduced shear stress for the Laplace pressure term.

Since shear stress due to the interface,  $\sigma_{int,xy}$ , can be written as the summation of  $\sigma_{v,xy}$  and  $\sigma_{L,xy}$ , Eqs. (12) and (14) lead to

$$\sigma_{int,xy} = \frac{\Gamma\phi}{r_0} [\sigma_{v,xy}^0(t/\tau_D, \gamma) + \sigma_{L,xy}^0(t/\tau_D, \gamma)]. \quad (15)$$

This indicates that plots of  $\sigma_{int,xy}/(\Gamma\phi/r_0)$  versus  $t/\tau_D$  make a single curve at each  $\gamma$  independently of  $\Gamma$ ,  $\phi$  and  $r_0$ .

## 2.2 Stress Relaxation of Blends with Polydisperse Droplets

Polymer blends include droplets with various sizes. Even if the droplet size distribution is narrow, for example,  $r_v/r_n = 1.20$ , the droplet size distribution can affect results of the stress relaxation for blends<sup>14)</sup>, where  $r_n$  represents the number average radius of droplets defined by

$$r_n = \sum_{i=1}^N r_i / N.$$

Therefore, it is necessary to consider the droplet size distribution when the stress relaxation of polymer blends is

investigated. In this case, Eq. (15) should be modified to express contribution from various sizes of droplets. Shear stress  $\sigma_{i,xy}$  arising from interface of an droplet in a blend with radius  $r_i$  and volume fraction  $\phi_i$  can be written using Eq. (15) as

$$\sigma_{i,xy} = \frac{\Gamma \phi_i}{r_i} \left[ \sigma_{v,xy}^0(t/\tau_{D,i}, \gamma) + \sigma_{L,xy}^0(t/\tau_{D,i}, \gamma) \right], \quad (16)$$

where  $\tau_{D,i}$  represents the relaxation time of the droplet and is given by

$$\tau_{D,i} = \frac{r_i \eta_m (19K + 16)(2K + 3 - 2\phi(K - 1))}{4\Gamma (10(K + 1) - 2\phi(5K + 2))}. \quad (17)$$

Equation (17) is a direct extension of Eq. (2) which gives the averaged relaxation time for droplets in blends. In Eq. (17), the  $\phi$  dependence is assumed to be the same as Eq. (2) in order to take influence of surrounding droplets on the  $i$ -th droplet into account. In addition, the proportionality is kept between the relaxation time and the droplet radius ( $\tau_{D,i} \propto r_i$ ). Moreover, volume-average of  $\tau_{D,i}$  is equal to  $\tau_D$ , i.e.,

$$\left( \sum_{i=1}^N \phi_i \tau_{D,i} \right) / \phi = \tau_D.$$

Because of the above reasons, Eq. (17) may be a good approximation. The same equation as Eq. (17) was used to evaluate stress due to the Laplace pressure term for polydisperse droplets in our previous study although it was not clearly mentioned.<sup>8)</sup>

Neglecting interaction between droplets, the total shear stress due to  $N$  droplets in the blend can be written as

$$\sigma_{\text{int},xy} = \sum_{i=1}^N \sigma_{i,xy} = \sum_{i=1}^N \frac{\Gamma \phi_i}{r_i} \left[ \sigma_{v,xy}^0(t/\tau_{D,i}, \gamma) + \sigma_{L,xy}^0(t/\tau_{D,i}, \gamma) \right]. \quad (18)$$

This leads to

$$\sigma_{\text{int},xy} = \frac{\Gamma \phi}{r_v} \sum_{i=1}^N \frac{(r_i/r_v)^2}{\sum_{j=1}^N (r_j/r_v)^3} \left[ \sigma_{v,xy}^0 \left[ (t/\tau_D)(r_v/r_i), \gamma \right] + \sigma_{L,xy}^0 \left[ (t/\tau_D)(r_v/r_i), \gamma \right] \right], \quad (19)$$

where a relation

$$\phi_i / \phi = r_i^3 / \sum_{j=1}^N r_j^3$$

is used. Equation (19) means that plots of  $\sigma_{\text{int},xy} / (\Gamma \phi / r_v)$  versus  $t/\tau_D$  make a single curve for each  $\gamma$  independently of  $\Gamma$ ,  $\phi$  and  $r_v$ , provided that reduced droplet size distribution  $r_i/r_v$  is independent of  $\Gamma$ ,  $\phi$  and  $r_v$ .

### 3. EXPERIMENTAL

We used PIB (Polyscience Co., Ltd.) and PDMS (Shin-Etsu Chemical Co., Ltd.) as component polymers. The zero shear viscosity of PIB and PDMS at 23 °C are 87.8 Pa•s and  $1.08 \times 10^3$  Pa•s, respectively, and the ratio of the zero shear viscosity is given by  $K = 0.081$ . The interfacial tension between the two components is 3.1 mNm<sup>-1</sup>, which is measured by the Pendant drop method at 23 °C. Blending was done by a stirrer followed by pre-shear in a rheometer. Blend ratios were PIB/PDMS = 10/90 and 20/80 (wt/wt). In these blends, minor PIB phase makes the droplet phase in PDMS matrix. The volume fraction  $\phi$  of the droplet phase, which is evaluated assuming the additivity of volume, is  $\phi = 0.108$  for 10/90 blend and  $\phi = 0.214$  for 20/80 blend.

The dynamic measurement in the linear viscoelastic region and the stress relaxation measurement under large step shear strains were carried out with ARES (Rheometric Scientific) using 25 mm  $\phi$  and 0.1 rad cone and plate geometry. Before the measurements for the blends, pre-shear was applied until steady state is reached. Pre-shear rates  $\dot{\gamma}$  are  $\dot{\gamma} = 0.12$  s<sup>-1</sup>, 0.25 s<sup>-1</sup> and 0.60 s<sup>-1</sup> for 10/90 blends and  $\dot{\gamma} = 0.25$  s<sup>-1</sup> for 20/80 blend. Step shear stains for the stress relaxation measurements were up to 4.5. Breakup and coalescence of droplets hardly occur in these stains.

### 4. RESULTS AND DISCUSSION

Figure 1 shows angular frequency  $\omega$  dependencies of dynamic moduli  $G'$  and  $G''$  for the PIB/PDMS = 10/90 blend after the pre-shear of  $\dot{\gamma} = 0.25$  s<sup>-1</sup> (symbols), and the components PDMS (broken lines) and PIB (thin solid lines). The  $\omega$  dependencies of  $G'$  and  $G''$  calculated by the Palierne theory<sup>1,2)</sup> with  $r_v = 7.1$   $\mu\text{m}$ , which give the best fit with the experimental data, are also plotted (thick solid lines). At lower  $\omega$  than the relaxation of the PDMS, both experimental and calculated results for the blend exhibit a shoulder in  $G'$ , which is the typical behavior of polymer blends with  $K \leq 1$ . The appearance of the shoulder is attributed to relaxation due to deformation and recovery of droplets caused by the interfacial tension between two phases.<sup>2,20)</sup>

Table I summarizes  $r_v$  determined by fitting the calculated results of the Palierne theory<sup>1,2)</sup> with the experimental results of  $G'$  and  $G''$  for the PIB/PDMS = 10/90 blends with various pre-shear rate  $\dot{\gamma}$  and the PIB/PDMS = 20/80 blend with  $\dot{\gamma} = 0.25$  s<sup>-1</sup>. The relaxation time  $\tau_D$  evaluated using Eq. (2) is also shown in Table I. The  $\dot{\gamma}$  dependence of  $r_v$  determined from Table I is

$r_v \propto \dot{\gamma}^{-0.9}$  for the PIB/PDMS = 10/90 blends, which agrees with the experimental results in “textured region” under steady shear flow for blends with  $K < 1$ .<sup>20,21</sup> This indicates that the blends in the present study are pre-sheared in the “textured region”. The experimental results in the “textured region” show that droplet size distribution  $r_v/r_n$  is less than 1.3.<sup>20,21</sup> This  $r_v/r_n$  value is not considered to be monodisperse in the stress relaxation measurements<sup>14</sup>) and we have to compare our experimental results with the prediction for the polydisperse droplets (i.e., Eq. (19)) although our blends are expected to have  $r_v/r_n$  rather small.

Figure 2 shows stress relaxation modulus  $G(t, \gamma)$  at various step strains  $\gamma$  as functions of time  $t$  for the PIB/PDMS = 10/90 blend after the pre-shear of  $\dot{\gamma} = 0.25 \text{ s}^{-1}$ . Plateaus and subsequent relaxations due to the interfacial tension are observed in similar and longer time regions as observed in Fig. 1. The height of the plateau at short and intermediate times decreases with increasing  $\gamma$ , while the total time necessary to complete relaxation increases with increasing  $\gamma$ . The same behavior is observed for the stress relaxation under large step shear strains for a 20/80 (wt/wt) blend of polystyrene/polycarbonate.<sup>17</sup>) It is known that elasticity of components affects the stress relaxation for polymer blends at times shorter than the relaxation time of components since the height of the plateau due to the interface is much lower than the plateau modulus due to the entanglement of polymer chains. Therefore, we have to subtract the effect of the relaxation modulus of components in order to extract relaxation modulus  $G_{\text{int}}(t, \gamma)$  due to the interfacial contribution and to apply the theoretical expressions for mixtures of two Newtonian fluids. In stress

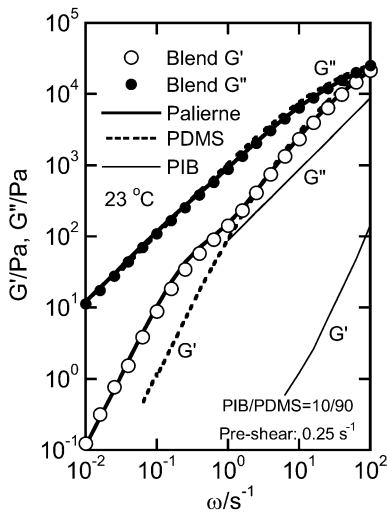


Fig. 1. Dynamic moduli for the PIB/PDMS = 10/90 blend after the pre-shear of  $\dot{\gamma} = 0.25 \text{ s}^{-1}$  and its components at 23 °C. The predicted dynamic moduli by the Paliere theory with volume-averaged radius of droplets  $r_v = 7.06 \text{ }\mu\text{m}$  are shown by the thick solid lines.

relaxation measurements for immiscible polymer blends, the linear additivity rule

$$G_{\text{int}}(t, \gamma) = G(t, \gamma) - [(1 - \phi)G_m(t, \gamma) + \phi G_d(t, \gamma)] \quad (20)$$

is known to be a good approximation<sup>8</sup>), where  $G_m(t, \gamma)$  represents the relaxation modulus of matrix phase and  $G_d(t, \gamma)$  the relaxation modulus of droplet phase. We used Eq. (20) to extract  $G_{\text{int}}(t, \gamma)$  from  $G(t, \gamma)$  obtained in the blends.

Figure 3 shows time dependence of  $G_{\text{int}}(t, \gamma)$  for PIB/PDMS = 10/90 blend after the pre-shear of  $\dot{\gamma} = 0.25 \text{ s}^{-1}$ . Since the relaxation time of PIB is much shorter than the relaxation time of the blend due to the interface as shown in Fig. 1,  $G_{\text{int}}(t, \gamma)$  is determined by Eq. (20) neglecting  $G_d(t, \gamma)$ . In Fig. 3,  $G_{\text{int}}(t, \gamma)$  at  $t < 0.4 \text{ s}$  is not shown since  $G_{\text{int}}(t, \gamma)$  is much smaller than  $(1 - \phi)G_m(t, \gamma)$ , and thus small experimental error in  $G(t, \gamma)$  and  $G_m(t, \gamma)$  causes large error in  $G_{\text{int}}(t, \gamma)$  at  $t < 0.4 \text{ s}$ . At  $t > 0.4 \text{ s}$ ,  $G_{\text{int}}(t, \gamma)$  exhibits the plateau and the subsequent relaxation due to the interface, which is expected from the behaviors of  $G(t, \gamma)$  in Fig. 2.

In Figs. 4 and 5, the reduced interface modulus  $G_{\text{int}}(t, \gamma)/(\Gamma\phi/r_v)$  is plotted against  $t/\tau_D$  at  $\gamma = 0.4$  and 4, respectively, for PIB/PDMS = 10/90 blends after various pre-shear rates. The plots for the

Table I. Volume-average droplet radius  $r_v$  and the relaxation time of the droplets,  $\tau_D$ , for the PIB/PDMS blends.

sample	$\phi$	$\dot{\gamma}/\text{s}^{-1}$	$r_v/\mu\text{m}$	$\tau_D/\text{s}$
PIB/PDMS = 10/90	0.108	0.12	13	6.2
PIB/PDMS = 10/90	0.108	0.25	7.1	3.5
PIB/PDMS = 10/90	0.108	0.60	3.1	1.6
PIB/PDMS = 20/80	0.214	0.25	8.6	4.8

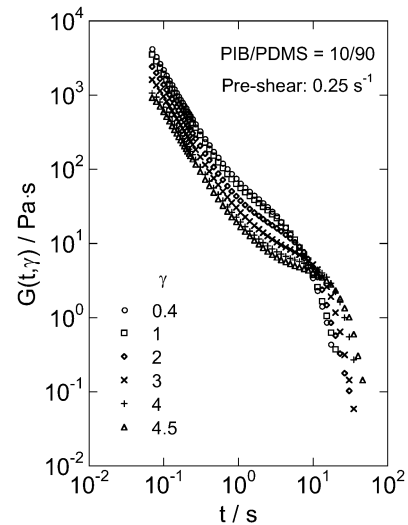


Fig. 2. Stress relaxation modulus  $G(t, \gamma)$  for the PIB/PDMS = 10/90 blend after the pre-shear of  $\dot{\gamma} = 0.25 \text{ s}^{-1}$  as a function of time  $t$  at various step shear strains  $\gamma$  at 23 °C.

blends after various pre-shear rates coincide fairly well. Such a coincidence are also observed in the plots for the other  $\gamma$ . The coincidence agrees with the prediction by Eq. (19). This indicates that the droplet size distribution around  $r_v$  is similar in the blends after various pre-shear rates and that the linear relaxation time  $\tau_D$  can reduce the time scale of the stress relaxation under large step shear strains where the relaxation modulus exhibits significant  $\gamma$  dependence. It should be noted that  $\tau_D$  is shorter than the total time necessary to complete the relaxation at large  $\gamma$ . The results in Figs. 4 and 5 mean that  $\tau_D$  is the common time scale to reduce the stress relaxation at various  $\gamma$  although the delay and increase in the total time of the relaxation is inherent in the  $\gamma$ -dependence. The coincidence also implies that interactions between droplets are not significant in the blends, or that the contribution from the interaction to the

stress is reduced by the same factors since Eq. (19) is derived neglecting the interactions.

Figure 6 shows the plots of  $G_{int}(t,\gamma)/(\Gamma\phi/r_v)$  versus  $t/\tau_D$  at  $\gamma=4$  for PIB/PDMS = 10/90 and 20/80 blends after pre-shear of  $\dot{\gamma}=0.25\text{ s}^{-1}$ . The data for both blends agree each other fairly well. This indicates that Eq. (19) is applicable for blends with different  $\phi$  and thus the interaction between droplets is negligible or the contribution from the interaction can be reduced by the same factors even for the blend with  $\phi=0.214$ . It should be noted that more precise experiments may reveal contributions from higher order terms of  $\phi$  since the experimental error of the stress relaxation measurements in the

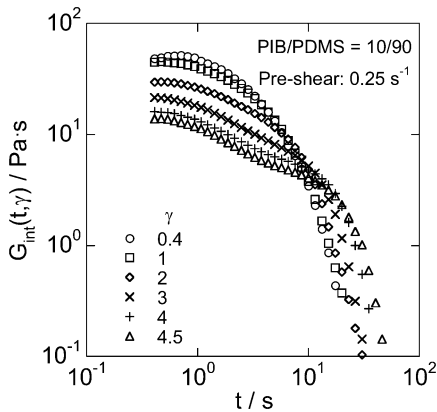


Fig. 3. Stress relaxation modulus due to the interface,  $G_{int}(t,\gamma)$ , for the PIB/PDMS = 10/90 blend after the pre-shear of  $\dot{\gamma}=0.25\text{ s}^{-1}$  as a function of time  $t$  at various step shear strains  $\gamma$  at 23 °C.

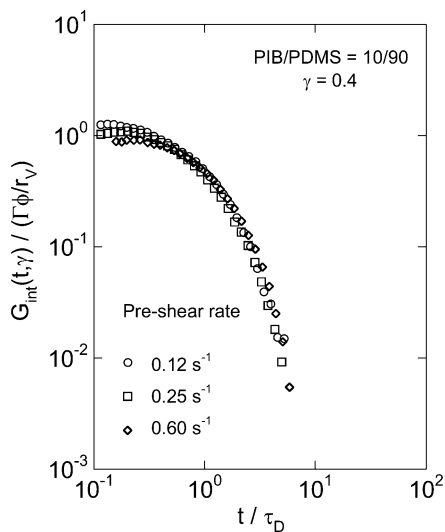


Fig. 4. Reduced interface modulus  $G_{int}(t,\gamma)/(\Gamma\phi/r_v)$  plotted against  $t/\tau_D$  at  $\gamma=0.4$  for the PIB/PDMS = 10/90 blends after various pre-shear rates.

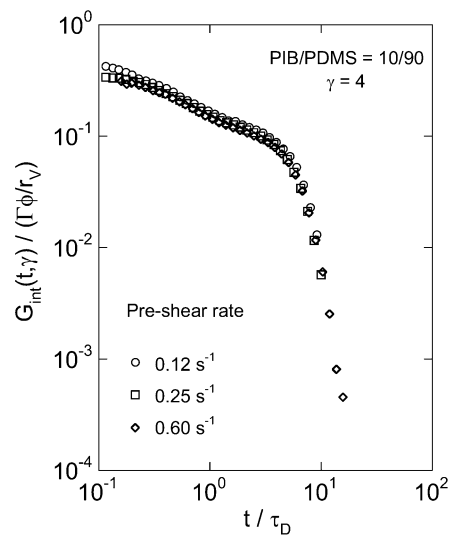


Fig. 5. Reduced interface modulus  $G_{int}(t,\gamma)/(\Gamma\phi/r_v)$  plotted against  $t/\tau_D$  at  $\gamma=4$  for the PIB/PDMS = 10/90 blends after various pre-shear rates.

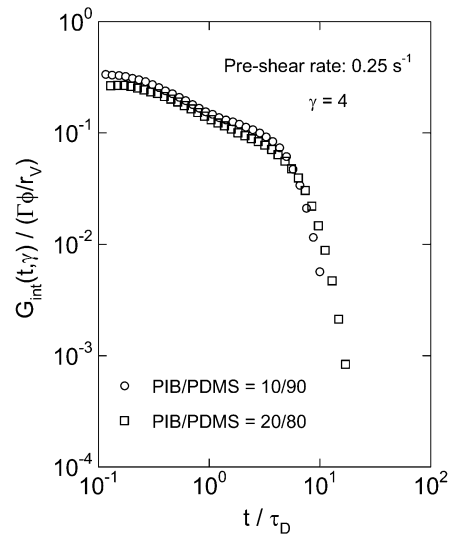


Fig. 6. Reduced interface modulus  $G_{int}(t,\gamma)/(\Gamma\phi/r_v)$  plotted against  $t/\tau_D$  at  $\gamma=4$  for the PIB/PDMS = 10/90 and 20/80 blends after the pre-shear of  $\dot{\gamma}=0.25\text{ s}^{-1}$ .

present study is rather large and around 20 %. Small effects of different  $\phi$  may exist but are not recognizable in Fig. 6 and the stress relaxation data for other  $\gamma$ . Another investigation is necessary to reveal such small effects, which may come from higher order terms of  $\phi$ .

## 5. CONCLUSIONS

We measured shear relaxation modulus  $G(t, \gamma)$  under large step shear strains  $\gamma$  for PIB/PDMS = 10/90 (wt/wt) and 20/80 (wt/wt) blends with the viscosity ratio  $K = 0.081$ . For the PIB/PDMS = 10/90 blend, the volume-average droplet radius is varied by applying pre-shear with various shear rates. The contribution of droplet/matrix interface to the relaxation modulus of the blends,  $G_{\text{int}}(t, \gamma)$ , is evaluated by subtracting the shear relaxation modulus of the matrix according to the volume additivity of the relaxation moduli.

The reduced plots of  $G_{\text{int}}(t, \gamma)/(\Gamma \phi / r_v)$  versus  $t/\tau_D$  for the blends with various droplet size and different volume fractions of droplets coincide well at each  $\gamma$ . This indicates that the time scale of the stress relaxation due to the interface can be reduced by  $\tau_D$  even in non-linear region. In addition, this coincidence agrees with the theoretical prediction based on the expression for mixtures of two Newtonian fluids<sup>9,10</sup>, which does not consider interactions between droplets. It is suggested that contribution from the interactions to the stress can be neglected in the present blends or that the contribution is also reduced by  $\Gamma \phi / r_v$  and  $\tau_D$ .

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