Effects of compatibilizer on immiscible polymer blends near phase inversion

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(Received 4 August 2006; final revision received 22 April 2007)

Synopsis

We consider the effects of adding a PIB-PDMS diblock copolymer as a compatibilizer in model blends composed of polyisobutylene (PIB) and polydimethylsiloxane (PDMS). The ratio of PIB to PDMS was varied from 20:80 to 80:20 and, hence, these blends are dubbed "concentrated" blends. Most experiments were conducted on blends containing 0.01 or 0.1 wt. % compatibilizer. All blends had a droplet-matrix morphology, with the minor phase being the drop phase; thus, phase inversion occured when PIB and PDMS were in a 50:50 ratio. Previously, we have studied effects of compatibilizer in "dilute" blends with PIB and PDMS in a 10:90 ratio. Much of the rheological behavior of the concentrated blends studied here is found to be qualitatively similar to that of dilute blends: compatibilizer increases the terminal complex viscosity, the terminal relaxation time, steady shear viscosity, and the ultimate recovery upon cessation of shear. However, there are two noteworthy differences. The first is that in blends in which PIB forms the continuous phase, the compatibilizer can suppress coalescence of the PDMS drops. Therefore, rheological properties that depend on drop size, e.g., relaxation time or ultimate recovery, are correspondingly affected. Second, the compatibilizer increases the viscosity, especially the terminal complex viscosity, of the concentrated blends far more than it does in dilute blends. This can be interpreted in terms of a partial immobilization of drop surfaces by the compatibilizer. Indeed, in blends with PIB as the continuous phase, the viscosity is only slightly lower than of a suspension of rigid spheres, suggesting that the compatibilizer immobilizes the interface almost completely. © *2007 The Society of Rheology.* [DOI: 10.1122/1.2742391]

I. INTRODUCTION

Block copolymers are often used to promote blending of immiscible homopolymers. In this role, block copolymers (bcps) are often called "compatibilizers": agents that make thermodynamically immiscible phases more "compatible." This paper is one of a series of papers on the rheological properties of model compatibilized blends. The earlier papers described experiments on blends usually containing 10% by weight of the dispersed phase PIB in PDMS, and up to 1% by weight of a PIB-PDMS diblock copolymer as compatibilizer. Due to the relatively low volume fraction of drops, those blends are called "dilute" blends in this paper. Broadly speaking, the results on dilute blends with 10 wt % PIB may be summarized as follows: Addition of compatibilizer (1) makes the blends more viscous: the terminal complex viscosity as well as steady shear viscosity increase slightly [Velankar *et al.* (2004a)], (2) makes the blends more elastic: the first normal stress difference and ultimate recovery increase [Wang and Velankar (2006b)], (3) increases all timescales: relaxation times increase, retardation times increase [Velankar *et al.* (2001, 2004a); Wang and Velankar (2006b)].

This paper was motivated by two observations. The first was that compatibilized blends containing equal weight fractions of PIB and PDMS had remarkably high viscosities [Wang (2005)]. A small increase in viscosity due to compatibilizer was documented in our earlier experiments on dilute blends [Velankar *et al.* (2004a)]; however, in blends with nearly equal PIB and PDMS, as little as 0.2% compatibilizer increased the viscosity by a factor of 4 [Wang (2005)]. The second observation was that the PIB-PDMS diblock compatibilizer used in these blends suppresses coalescence when PIB is the continuous phase, but not when PDMS is the continuous phase. The immediate suspicion then was that these two observations are related: in blends with nearly equal amounts of PIB and PDMS, the compatibilizer changes the morphology in some way, and that morphological change is responsible for the large increase in viscosity.

We therefore undertook a systematic study of blends with nearly equal volume fractions of the two phases. Rheological experiments on blends with exactly equal volume fraction of the two phases were found to be difficult to reproduce (this will be discussed further) and, hence, most experiments were conducted on blends with either 40% or 60% of PIB. Such blends will be called "concentrated" blends in this paper. We ask the following specific questions in this paper:

- Does the compatibilizer change the morphology of the blends when the two components have nearly equal volume fraction? In particular, does the compatibilizer shift the phase inversion composition? If not, is there some other significant change in the morphology, e.g., cocontinuity, or fibril formation?
- Are morphological changes, if any, responsible for the above-mentioned high viscosity of concentrated blends? If not, what is the mechanism by which compatibilizer increases the viscosity so much?
- In addition to the viscosity, are other rheological properties also strongly affected by compatibilizer in concentrated blends?

II. MATERIALS AND METHODS

The blends under investigation consisted of poly(dimethylsiloxane) (PDMS, Rhodorsil 47V60000 from Rhodia Chemicals, MW roughly 150 000 g/mol) and poly(isobutylene) (PIB 32, Soltex Chemicals, MW roughly 1300 g/mol). A diblock copolymer of PIB and PDMS ($M_{w,\mathrm{PIB}}=6150$ g/mol and $M_{w,\mathrm{PDMS}}=8000$ g/mol) was used as a compatibilizer. This same diblock has been used in previous studies [Velankar *et al.* (2001, 2004a)]. All experiments were conducted at 25 °C, at which the viscosities of the bulk components are essentially equal. At 25 °C the viscosities of PDMS and PIB are 56.2 and 57.3 Pa s, respectively, resulting in a viscosity ratio, p, of almost exactly 1. Thus, the phase inversion composition in uncompatibilized blends is expected to be 50 vol % of PIB. Both components are nearly Newtonian at 25 °C, with PDMS having a relaxation time on the order of 0.01 s and PIB even smaller.

Since we are interested in questions of phase continuity, it is important to control the volume fractions of the PIB and PDMS (rather than the weight fractions as in the previous papers). However, since the density of the compatibilizer is not known exactly, it is still convenient to control the compatibilizer on a weight basis. Accordingly, samples will be designated by $B\phi_{\mathrm{PIB}}$-w_{comp} where ϕ_{PIB} is the volume fraction of PIB on a compatibilizer-free basis, and w_{comp} is the overall weight % of compatibilizer. For ex-

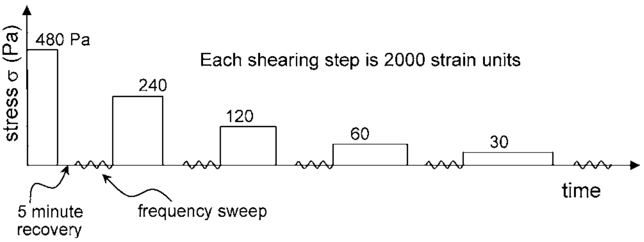

FIG. 1. Schematic of a typical sample shear history.

ample, 1 gram of B40-0.1 consists of 0.386 g (0.427 ml) of PIB, 0.613 g (0.639 ml) of PDMS, and 0.001 g of compatibilizer. Blends ranging from 20 to 80 volume percent PIB and 0 to 0.5 wt % compatibilizer were tested, however, a majority of the discussion below is restricted to B40-0, B60-0, B40-0.1, and B60-0.1 blends. It was verified previously that such small levels of compatibilizer do not affect the bulk rheology of the two phases significantly [Velankar *et al.* (2004a)]. Following the above nomenclature, the blends studied previously, which had 10 wt % PIB (i.e., 10.7 vol % PIB), will be denoted B11 blends.

Blends were prepared by hand-mixing the appropriate amounts of compatibilizer and bulk materials with a spatula for 10 min and then degassing the sample under vacuum. Experiments were performed in a TA Instruments AR2000 stress-controlled rheometer using a 40 mm diameter/1° cone and plate geometry and a Peltier cell to maintain the sample temperature at 25 °C. The shear history of the samples is shown in Fig. 1. Samples were sheared at 480 Pa for 2000 strain units and the recovery upon cessation of shear was measured. A dynamic frequency sweep at 25% strain was performed. The sample was then sheared at 240 Pa for 2000 strain units followed by recovery and another frequency sweep experiment. This sequence was repeated three more times, with shearing occurring at 120, 60, and 30 Pa, respectively. The rheology of the sample was confirmed to be unvarying over the timescale of a frequency sweep.

III. RESULTS

A. Morphology and phase continuity

In our previous research on B11 blends, we did not pay much attention to the morphology since, in dilute blends, one always obtains a droplet-matrix morphology with the minority phase being the drops. In this paper, we are principally concerned with blends that contain either 40% or 60% PIB. Since the volume fractions of the immiscible phases are so close to each other, it cannot be presumed that the morphology remains droplet-matrix, or that the minority phase remains the dispersed phase. Therefore, at least a qualitative examination of the morphology is essential.

Unfortunately, since both PIB and PDMS are liquid at room temperature and have very low glass transition temperatures, this system is ill-suited for electron microscopy, or any method that requires the sample to be "solidified". Also, because the blends are not dilute, they scatter strongly and, hence, optical microscopy during shearing is quite difficult. We have conducted optical microscopy under quiescent conditions of samples placed between glass slides separated by a thin spacer. Images of both as-mixed blends as well as blends withdrawn from the rheometer after shearing always show droplet-matrix

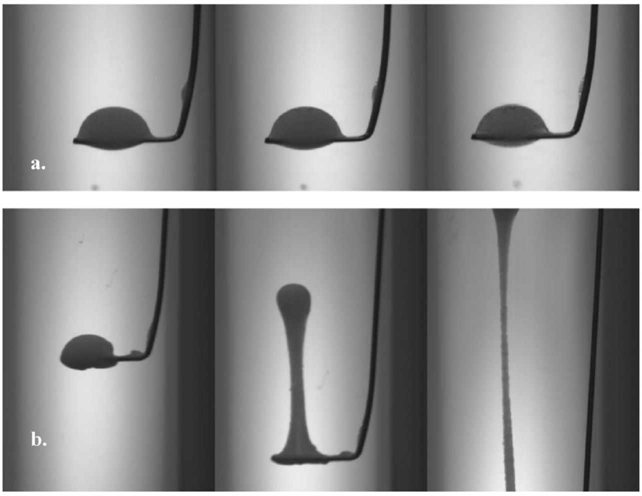

FIG. 2. Tests of phase continuity by immersing blends in silicone oil (a) B60-0.1, (b) a B40-0.1.

morphologies. Yet, from such images, it is not obvious which phase forms the drops. Since the issue of phase continuity is extremely important when interpreting the rheology, we tested this in more detail.

The standard method to test phase continuity in oil/water emulsions is to inject a small sample of the emulsion into a container of water. If the emulsion has water as the continuous phase, the oil droplets disperse rapidly, if oil is the drop phase, the emulsion sample does not disperse rapidly. Due to the high viscosity of the polymer blends studied here, this test cannot be applied easily since it is difficult to inject a PIB/PDMS blend into, say, pure PIB due to the high viscous stresses involved. Fortunately, a selective solvent of low viscosity is available: silicone oil (low-MW PDMS) is miscible only with the PDMS in the blend. Therefore, the following procedure was developed. A small drop of the blend was placed on the tip of a bent wire and then gently immersed in silicone oil of viscosity 1 Pa s. In all blends with PIB as the majority phase, the drop of blend remained on the needle, with only a slight change in shape due to interfacial tension and buoyancy [Fig. 2(a)]. In contrast, in blends with PDMS as the majority phase, the drop of the blend rose upwards in a plume due to buoyancy [Fig. 2(b)], leaving behind a "trail." In some cases when drops of the blend were large (e.g., in uncompatibilized blends) single drops were evident in the rising plume. The above observations prove beyond doubt that if $\phi_{\mathrm{PIB}} \leqslant 40\%$, PIB becomes the drop phase, whereas if $\phi_{\mathrm{PIB}} \geqslant 60\%$, PDMS becomes the drop phase.

We have also conducted a similar experiment (bringing a blend in contact with pure PDMS or pure PIB) under an optical microscope. These experiments also confirm the above conclusion of phase continuity.

Similar to past publications in this series, the chief concern here is the rheological effects of adding compatibilizer and not the effect of compatibilizer on the drop sizes. Here we only mention that addition of compatibilizer reduces the drop size, and that B60 blends with compatibilizer have much smaller drops than B40 blends with compatibilizer. This is almost certainly attributable to the ability of the compatibilizer to suppress coalescence (discussed below).

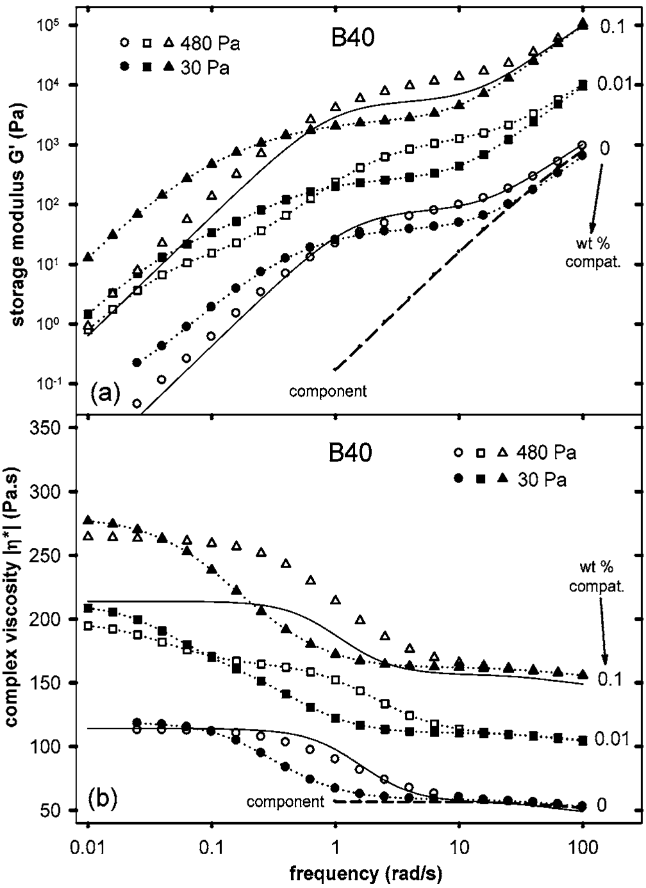

FIG. 3. Dynamic oscillatory properties of (a),(b) B40 blends, and (c),(d) B60 blends. Open and filled symbols refer to experiments after shearing at 480 Pa and 30 Pa, respectively. Solid lines are best fits of the Palierne model without interfacial viscoelasticity to the data at 480 Pa. For clarity, each curve in (a) and (c) has been shifted upwards by a factor of 10 with respect to the previous one; curves for B40-0 and B60-0 have not been shifted. For clarity, each curve in (b) and (d) has been shifted upwards by 50 Pa.s with respect to the previous one; curves for B40-0 and B60-0 have not been shifted.

To summarize, the morphology of the blends appears quite ordinary: (1) a droplet-matrix morphology is always obtained, at least under quiescent conditions, and unusual morphologies, e.g., cocontinuity or fiber-like morphologies do not occur; (2) blends do *not* show phase inversion, i.e., all blends with up to 40% PIB have PIB drops, and all blends with more than 60% PIB have PDMS drops.

Finally, we note that we have not tested the phase continuity of B50 blends. Since our system is equiviscous, we expect the phase inversion point to be around $\phi_{\mathrm{PIB}}=0.5$ [Paul and Barlow (1980)] and, hence, such blends may have not have a droplet-matrix morphology under flow. For example, Jansseune *et al.* (2003) observed a fibrillar morphology in PIB / PDMS near the phase inversion point at high shear rates.

B. Dynamic oscillatory experiments

Figures 3(a)–3(d) show the elastic modulus, G', and the magnitude of the complex

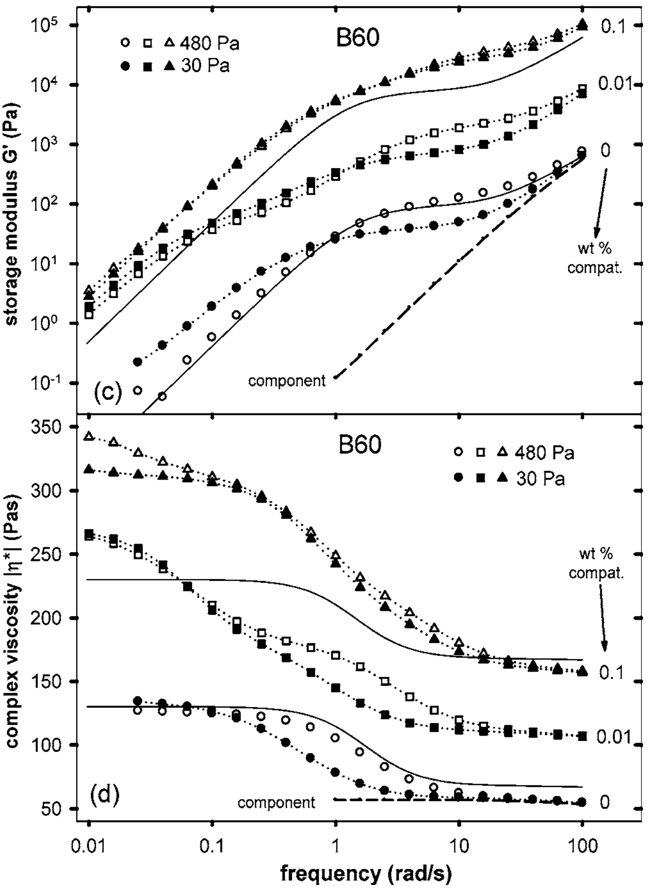

FIG. 3. (*Continued*).

viscosity, $|\eta^*|$, for the B40 and B60 blends. For clarity, only the data at the end of the highest stress (480 Pa) and lowest stress level (30 Pa) are shown. The curves at intermediate stresses lie between these limits in all cases.

We will discuss the behavior of B40 blends first. Consider first the lowest set of results in Figs. 3(a) and 3(b), which correspond to the uncompatibilized B40-0 blend. Comparing this blend with the volume-average of the components (dashed lines), the most notable feature is the relaxation process, manifested as shoulders in G' and $|\eta^*|$. Since this relaxation is absent in the components, it may be regarded as an interfacial relaxation process. This relaxation is well-known and arises from the deformation and relaxation of the droplets during the oscillatory experiment [Graebling *et al.* (1993b)]: at frequencies substantially above the shoulder the drops deform along with the applied oscillatory flow, whereas at substantially lower frequencies, the drops remain nearly-spherical due to interfacial tension. Dimensional analysis suggests that the relaxation time corresponding to this interfacial relaxation process scales as $(\eta_m R/\alpha) f(\phi_d, p)$, where η_m is the viscosity of the matrix, R is the mean radius of the drops, α is the interfacial tension, ϕ_d is the volume fraction of drops, and p is the ratio of the viscosity of the drops to that of the matrix. Detailed predictions of the function $f(\phi_d, p)$ are available [Oldroyd (1950); Palierne (1990)], and the Palierne model, in particular, has been commonly used in the literature [Graebling *et al.* (1993a); Vinckier *et al.* (1996)]. An example of a fit of the

Palierne model to the data for the B40-0 blend sheared at 480 Pa is shown in Figs. 3(a) and 3(b) (solid lines). Evidently, good fits can be obtained using R/α as the only fitting parameter. In the case of uncompatibilized blends, all quantities except R are fixed. Upon reducing the stress from 480 Pa to 30 Pa, drops grow by coalescence, and this is apparent as a shift of the relaxation process to lower frequencies as seen in Figs. 3(a) and 3(b).

Upon addition of a small amount, 0.01 wt %, of compatibilizer [the middle set of curves in Figs. 3(a) and 3(b)], the most obvious effect is the appearance of a second, much slower interfacial relaxation process, manifested by a second shoulder in G' and a corresponding shoulder in $|\eta^*|$ at low frequency. This slower relaxation has been seen previously [Riemann *et al.* (1997); Van Hemelrijck *et al.* (2004, 2005)] and has been attributed to flow-induced gradients in block copolymer concentration and, hence, flow-induced interfacial tension gradients on the interface. It is the relaxation of these gradients which is believed to cause the slow relaxation process: at frequencies well above the slow relaxation, the oscillatory shear is able to induce gradients in interfacial bcp concentration, whereas at much lower frequencies, the bcp remains nearly uniformly distributed on the interface. What is the mechanism by which the bcp remains at a uniform concentration over the drop surface at low frequencies? The first two possibilities, bulk diffusion of bcp or interfacial diffusion of bcp, seem unlikely since a previous calculation suggests that the diblock used here has a very low diffusivity [Velankar *et al.* (2001)]. The third possibility seems more likely: a Marangoni stress caused by the interfacial tension gradients acts tangentially along the interface to establish a uniform bcp concentration. In summary, two interfacial relaxation processes are evident in the presence of block copolymer, the faster one may be associated mainly with shape relaxation of the drops, and the slower one mainly with relaxation of interfacial tension gradients.

This effect of interfacial tension gradients causing two relaxation processes can be modeled by endowing the interface with interfacial viscoelastic properties. In the simplest case, one may define an interfacial dilation modulus [Wang and Velankar (2006b)]:

$$\beta = A\frac{\partial \alpha}{\partial A}, \tag{1}$$

where A is the area of the interface. The relaxation times of the two relaxation processes can then be shown [Jacobs *et al.* (1999); Wang and Velankar (2006b)] to be of the form $(\eta R/\alpha)f(\phi, p, \beta/\alpha)$. Corresponding expressions for the relaxation times are also available if other interfacial properties such as an interfacial shear modulus or an interfacial viscosity are considered [Oldroyd (1955); Jacobs *et al.* (1999)]. Using such expressions, one may then obtain the interfacial viscoelastic properties from the observed relaxation times [Riemann *et al.* (1997); Jacobs *et al.* (1999); Van Hemelrijck *et al.* (2004, 2005)]. Since both relaxation times are predicted to be proportional to drop size, one may expect that, with decreasing stress, coalescence would cause a shift in both the relaxation processes to low frequencies. Experimentally, however, comparing the results at 480 Pa vs 30 Pa, only the faster process is seen to shift to lower frequency with reducing stress. The slower process appears independent of stress. A similar insensitivity of the slow relaxation to drop size was noted previously [Van Hemelrijck *et al.* (2004, 2005)].

Upon further increase in the amount of compatibilizer to 0.05% (not shown), the slow relaxation moves to higher frequencies. At 0.1% compatibilizer [the topmost curves in Figs. 3(a) and 3(b)], the two shoulders merge together and are no longer evident separately. This convergence of the two relaxation processes with increasing compatibilizer content was also observed by Van Hemelrijck *et al.* (2004). The convergence may also be interpreted as an increase in interfacial dilational modulus with compatibilizer concentration since it has been shown that if the interfacial dilational modulus becomes comparable to the interfacial tension, the two relaxation times become comparable and only a single shoulder is visible in G' and $|\eta^*|$ [Jacobs *et al.* (1999)]. Thus, the dynamic oscillatory properties of blends with sufficiently large amounts of compatibilizer are qualitatively similar—i.e., show only a single shoulder in G' and $|\eta^*|$—to those of uncompatibilized blends [Velankar *et al.* (2001)]. Quantitatively, however, the Palierne model without interfacial viscoelasticity cannot fit the oscillatory moduli well; the best fit with α/R as the only fitting parameter greatly underestimates the strength of the interfacial relaxation process.

Finally, it must be emphasized that the apparently-single relaxation in B40-0.1 shifts to lower frequencies upon reducing stress. This suggests that flow-induced coalescence can still occur in B40-0.1. We will see significantly different behavior in the B60-0.1 blend below.

The above observations on B40 blends are all qualitatively similar to those discussed previously for B11 blends with compatibilizer. Evidently, moving from dilute B11 blends to concentrated B40 blends causes no qualitative change in the dynamic viscoelastic properties.

We now turn to B60 blends. The lowest set of curves in Figs. 3(c) and 3(d) show that the uncompatibilized B60-0 blend behaves very similarly to the B40-0 blend: a single relaxation process is evident, and it moves to lower frequencies upon reducing stress indicating flow-induced coalescence. Once again, the Palierne model without interfacial viscoelasticity predicts the moduli well with α/R as the only fitting parameter. The effect of addition of 0.01% compatibilizer on the B60 blend is also quite similar to that discussed above for B40-0.01: a second, slower relaxation process appears which is insensitive to stress.

Upon increasing the compatibilizer level to 0.1%, two relaxation processes are still visible, however they have nearly merged, as expected from the B40-0.1 blend above. Once again, the Palierne model without interfacial viscoelasticity greatly underpredicts the strength of the relaxation process. However, a significant difference emerges: the dynamic oscillatory properties become almost insensitive to stress. Since the dynamic moduli are directly related to the size of the drops, this suggests that the drop size does not increase upon reducing stress, i.e., the 0.1% block copolymer suppresses coalescence in the B60 blend.

To summarize the qualitative discussion of the dynamic oscillatory properties in this section: both uncompatibilized blends, B40-0 and B60-0, show a single interfacial relaxation process corresponding to the shape-relaxation of drops. This relaxation slows down with reducing stress, suggesting flow-induced coalescence. In both B40 as well as B60 blends, upon adding 0.01% compatibilizer, two interfacial relaxation processes are evident. The faster of these two processes slows down with decreasing stress, whereas the slower process seems insensitive to stress. At 0.1% compatibilizer the two relaxation processes merge, but differences between B40 and B60 blends are evident: in the B40-0.1, the relaxation slows down with reducing stress suggesting that the compatibilizer does not suppress coalescence. In contrast, in B60-0.1 the dynamic moduli appear insensitive to stress indicating that the compatibilizer is able to stop coalescence. This conclusion, that the compatibilizer can prevent coalescence when PIB is the continuous phase, but not when PDMS is the continuous phase, has been verified by direct visualization (see Sec. IV A).

Next we conduct a quantitative analysis of the oscillatory moduli. Only two aspects of the oscillatory measurements will be discussed: the magnitude of the terminal complex viscosity $|\eta_0^*|$, and the relaxation time of the interfacial relaxation.

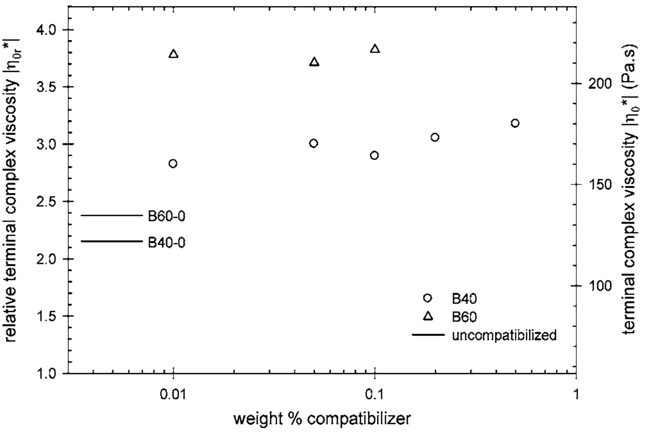

FIG. 4. Dependence of terminal complex viscosity on compatibilizer loading for B40 and B60 blends.

In most blends, $|\eta_0^*|$ was essentially independent of the stress prior to the oscillatory measurement [most of the differences in the $|\eta_0^*|$ after 480 Pa shearing vs after 30 Pa shearing in Figs. 3(b) and 3(d) are random experimental error and typically well within 10% of the average]. The only exception is B60-0.1 in which $|\eta_0^*|$ after the first two stresses [480 Pa shown in Fig. 3(d), and 240 Pa, not shown] was consistently higher than the $|\eta_0^*|$ after the three lower stresses. In all cases including B60-0.1, we have simply averaged the $|\eta_0^*|$ values at all stresses. These average values are plotted as a function of compatibilizer loading in Fig. 4 (referring to the right axis). The $|\eta_0^*|$ values can also be rendered dimensionless by a volume average of both components:

$$|\eta_{0r}^*| = \frac{|\eta_0^*|}{\phi_d \eta_d + \phi_m \eta_m}, \tag{2}$$

where $|\eta_{0r}^*|$ is the relative terminal complex viscosity of the blend, and η_d and η_m are the viscosities of the droplet phase and matrix phase, respectively. The denominator in Eq. (2) is the simplest means of estimating the bulk contribution to the viscosity of a two-phase blend. This estimate can be very poor if the viscosities of the two phases are highly mismatched, but in the present case, since $\eta_d \approx \eta_m$, the approximation works very well. In fact, going from $\phi_{\mathrm{PIB}}=0$ to $\phi_{\mathrm{PIB}}=1$, the denominator of Eq. (2) varies by less than 2%. The values of $|\eta_{0r}^*|$ thus calculated can be read off Fig. 4, referring to the left axis.

The most surprising observation is the large effect of the compatibilizer on the terminal complex viscosity, especially in the B60 blends. A modest increase in the terminal complex viscosity with compatibilizer was reported previously for the B11 blends [Velankar *et al.* (2004a)], but the effect of compatibilizer seems to be much larger in the concentrated blends here, e.g., in the B60 blend, as little as 0.01% compatibilizer raises the terminal complex viscosity by more than 60%. Further addition of compatibilizer has relatively little effect on the terminal complex viscosity. As mentioned above, the effects of compatibilizer may be modeled by endowing the interface with an interfacial dilation modulus. In the case of dilute emulsions, such models [Oldroyd (1955); Jacobs *et al.* (1999)] predict that, if the interfacial modulus is frequency-independent, the zero-shear viscosity approaches that of a suspension of rigid spheres, regardless of the *magnitude* of the modulus. This may explain why the terminal complex viscosity is the same at all compatibilizer loadings: the interfacial modulus may increase with increasing compatibi-

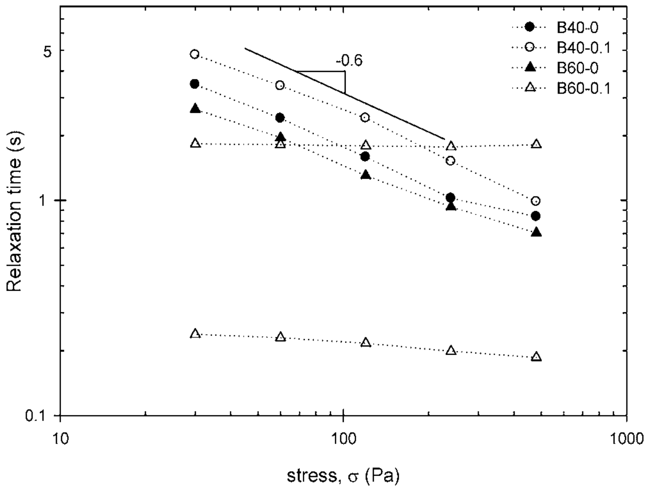

FIG. 5. Relaxation times of the interfacial relaxation process in blends. B40-0, B40-0.1, and B60-0 could all be fitted with a single relaxation time. B60-0.1 required two relaxation times; both are shown above.

lizer loadings, but the terminal complex viscosity remains unaffected. This will be discussed further in Sec. IV B.

Finally, it is of interest to examine the relaxation time of the blends quantitatively. For blends with 0.01% compatibilizer, this is difficult because, due to the very slow relaxation process, the terminal region is barely reached in the experimentally accessible frequency window. Therefore, the analysis for relaxation times is restricted only to blends with 0% and 0.1% compatibilizer. This analysis follows the procedure detailed previously [Velankar *et al.* (2004a); Wang and Velankar (2006a)]. Briefly, the interfacial contribution to the storage modulus is defined as

$$G'_{\text{interface}} = G'_{\text{measured}} - G'_{\text{component}} = G'_{\text{measured}} - G'_{\text{Palierne}}(\alpha = 0), \tag{3}$$

where $G'_{\text{component}}$ is the bulk contribution to the modulus, obtained from the Palierne model by setting interfacial tension equal to zero. $G'_{\text{interface}}$ can then be fitted very well by a sum of very few Maxwell modes [Secor (1994)]:

$$\log[G'(\omega)] = \log\left[\sum_{k=1}^{n} \frac{\omega^2 \exp(a_k + 2t_k)}{1 + \omega^2 \exp(2t_k)}\right]. \tag{4}$$

In the present case, B40-0, B60-0, and B40-0.1 can be fitted very well by a single Maxwell mode ($n=1$), whereas B60-0.1 requires two modes ($n=2$). As previously, internal consistency was tested by verifying that the $|\eta^*(\omega)|$ corresponding to the sum of Maxwell modes was in good agreement with the interfacial contribution to the complex viscosity measured experimentally. More details of this procedure have been presented previously [Velankar *et al.* (2004a); Wang and Velankar (2006a)].

Figure 5 plots the relaxation time of the interfacial relaxation process as a function of stress, σ, in the various blends. As discussed qualitatively above, in B40-0 and B60-0, the interfacial relaxation time increases as stress reduces. Figure 5 shows that the relaxation time has an approximately $\sigma^{-0.6}$ dependence on stress. In uncompatibilized blends, the drop size is proportional to the relaxation time and, hence, we conclude that $\mathrm{R} \propto \sigma^{-0.6}$ in both these blends. A similar dependence has been predicted by Vinckier *et al.* (1998) for a coalescence-limited morphology, albeit in a rate-controlled experiment.

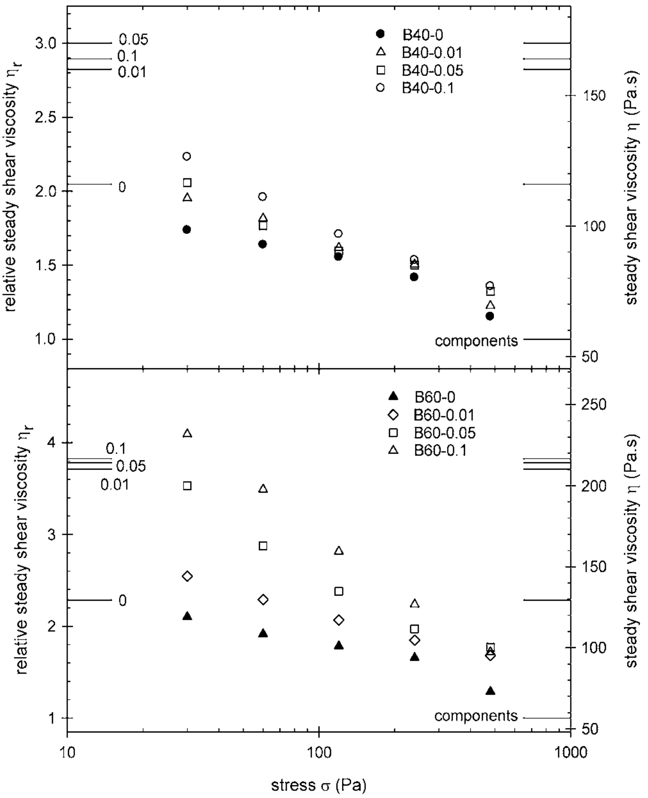

FIG. 6. Steady shear relative viscosity as a function of shear stress for $\phi_{\mathrm{PIB}}=0.40$ and 0.60. Relative terminal complex viscosities from dynamic oscillatory data are plotted as solid lines.

Addition of 0.1% compatibilizer to B40 raises the interfacial relaxation time by about 50% at all stresses. Such an increase of interfacial relaxation time with compatibilizer has been previously noted for B11 blends [Velankar *et al.* (2001, 2004a)]. The stress dependence of the relaxation time of B40-0.1 still remains approximately $\sigma^{-0.6}$. This increase in relaxation time with reducing stress indicates an increase in drop size with reducing stress, although there may not be an exact proportionality between drop size and relaxation time in compatibilized blends. For the B60-0.1 blend, a single Maxwell mode is insufficient to capture the interfacial relaxation, and hence the relaxation times of both modes are shown. As discussed qualitatively above, since the dynamic moduli were insensitive to stress, the relaxation times are insensitive to stress as well—a quantitative measure of coalescence suppression.

C. Steady shear viscosity and terminal complex viscosity

Both compatibilized as well as uncompatibilized blends were found to be shear-thinning. Since experiments were conducted at successively decreasing stresses, upon starting the shearing at a fixed stress level, the viscosity increased gradually to its steady state value at that stress. Typically, 100–400 strain units of shearing were required to reach the steady shear viscosity; compatibilized blends generally reached steady values at shorter shear strains than uncompatibilized ones. These steady shear values of the viscosity are plotted in Fig. 6 (referring to the right axis). Similar to Eq. (2), the steady shear values can also be rendered dimensionless:

$$\eta_r = \frac{\eta_b}{\phi_d \eta_d + \phi_m \eta_m}, \tag{5}$$

where η_b is the blend viscosity. These values of η_r can be read off the left axis of Fig. 6. Finally, the values of the terminal complex viscosity from Fig. 4 are also added to Fig. 6 as horizontal lines for comparison.

As in the previous section, the B40 blends are discussed first. Consider first the B40-0 blend which shows a steady shear viscosity that increases with decreasing shear stress. Shear-thinning in uncompatibilized droplet-matrix blends has been documented previously [Vinckier *et al.* (1996)], and is attributable to the deformation and velocity-alignment of the drops subjected to shear flow. Theory predicts that the magnitude of shear thinning of blends without compatibilizer is governed by the capillary number [Frankel and Acrivos (1970); Choi and Schowalter (1975)]:

$$\mathrm{Ca} = \frac{\text{viscous stress}}{\text{interfacial stress}} = \frac{\sigma R}{\alpha}. \tag{6}$$

In most previous publications, the viscous stress has been written as $\eta_m \dot{\gamma}$, however, the above definition is more appropriate in stress-controlled experiments. The previous section showed that, for the uncompatibilized B40-0 and B60-0 blends, $R \propto \sigma^{-0.6}$ is approximately correct. Therefore, Eq. (6) suggests the approximate dependence of $\mathrm{Ca} \propto \sigma^{0.4}$, i.e., Ca decreases as stress decreases. Therefore with reducing stress, the drops deform less, resulting in an increased blend viscosity [Frankel and Acrivos (1970); Choi and Schowalter (1975)]. The η_r vs stress curve seems to approach $|\eta_{0r}^*|$ at low stresses, yet, a plateau viscosity, which would be indicative of the zero-shear value, is not apparent up to the lowest stress value of 30 Pa.

With addition of compatibilizer, all the steady shear viscosities increase. As explained previously [Velankar *et al.* (2004a)], this increase in viscosity may be attributed to flow-induced gradients in compatibilizer concentration: the corresponding Marangoni stresses and gradients in capillary pressure resist flow, and hence increase the viscosity of the blend. In the B40 blends with compatibilizer (as well as B20 and B30 blends with compatibilizer, not shown), the increase in viscosity with compatibilizer was greatest at low stresses. There seems to be a significant discrepancy between the viscosity measured at the lowest stress level and $|\eta_0^*|$. Certainly, η must approach $|\eta_0^*|$ at sufficiently low stress, yet from Fig. 6(a), it appears that 30 Pa is far into the shear-thinning region. A similar, although smaller, discrepancy is apparent upon comparing the steady shear and terminal complex viscosities of the B30 compatibilized blends (not shown).

Next we consider the B60 blends. The B60-0 blend behaves quite similar to the B40-0 blend although the actual values of the viscosity are somewhat higher for the B60-0. Upon addition of a small amount (0.01%) of compatibilizer, the behavior is similar to that of the B40-0.01 noted above: η increases at all stress levels, but there is still a large discrepancy between η at 30 Pa and $|\eta_0^*|$, indicating that shear-thinning starts at much lower stresses. Upon increasing the compatibilizer loading, two quantitative differences appear: first, the viscosity increases to much higher values than in B40-0.1, second, the η vs stress curve does seem to approach $|\eta_0^*|$. In fact, at 30 Pa, the steady shear viscosity seems to be larger than the terminal complex viscosity. This does not appear to be an error: three independent measurements on B60-0.1, as well as measurements on B70-0.1 and B80-0.1 blends, show the same unusual feature.

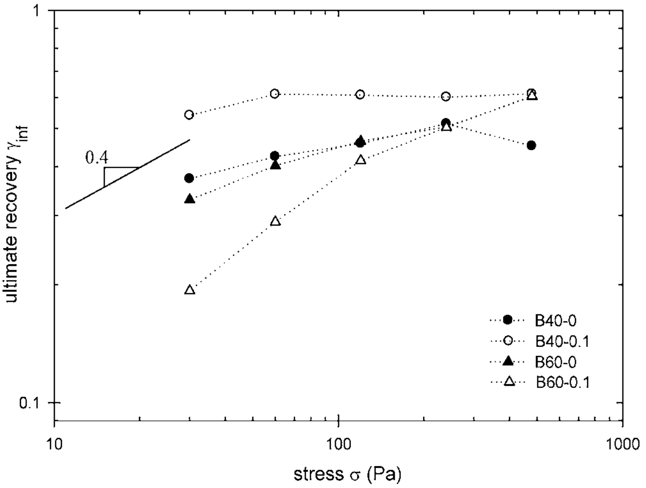

FIG. 7. Ultimate recovery for B40 and B60 blends.

Finally, it is interesting to note that in B60 blends, the terminal complex viscosity is independent of compatibilizer content (previous section and Fig. 4), whereas steady shear viscosity increases with compatibilizer (Fig. 6). This will be discussed further in Sec. IV B.

D. Recovery

During steady shear, the drops of an uncompatibilized blend deform and orient along the flow direction. After cessation of shear, these deformed drops retract back into spherical shapes and induce creep recovery of the blends. In previous experiments on uncompatibilized blends, the creep recovery upon cessation of steady shear was found to be well-described by single-exponential kinetics with only two parameters: the ultimate recovery γ_∞, and the time required for recovery [Vinckier *et al.* (1999); Wang and Velankar (2006a)]. Thus, by fitting the recovery curves to a single-exponential, the recovery time could be obtained as the only fitting parameter (ultimate recovery is not a fitting parameter since it can be obtained directly from the recovery vs time data). Experiments on B11 blends show that the recovery of compatibilized blends is more complicated and cannot be described by a single exponential process [Wang and Velankar (2006b)]. Our results here agree with the previous observations: B40-0 and B60-0 can be well-represented by single-exponential kinetics, but the compatibilized blends cannot. Therefore we will only discuss one parameter associated with the creep recovery: the ultimate recovery γ_∞.

Figure 7 shows γ_∞ for the B40 and B60 blends. Consider first B40-0 and B60-0 uncompatibilized blends. The linear viscoelastic theory of the recovery of droplet-matrix blends predicts that γ_∞ is proportional to the capillary number prior to cessation of shear [Vinckier *et al.* (1999); Wang and Velankar (2006a)]. Based on the discussion in the previous section, we expect $\gamma_\infty \propto \mathrm{Ca} \propto \sigma^{0.4}$. However, experimentally, a weaker stress dependence is observed, perhaps because the actual Ca values are too large for the linear theory to hold quantitatively. These observations agree well with our previous research on uncompatibilized blends that shows that the linear viscoelastic theory does not predict the ultimate recovery well [Wang and Velankar (2006a)].

Addition of compatibilizer to the B40 blend increases γ_∞ at all stress levels, consistent with our previous results on compatibilized B11 blends [Wang and Velankar (2006b)]. Briefly, the mechanism proposed previously was as follows: for a compatibilized droplet-matrix blend under steady shear, the applied flow convects the compatibilizer to the tips of the drops, giving the tips a lower interfacial tension. This non-uniformity in interfacial tension affects the retraction of the drops upon cessation of shear and, hence, the recovery. The interplay between various effects (Marangoni stresses, gradients in capillary pressure, change in the average interfacial tension during retraction) is complex [Velankar *et al.* (2004b); Wang and Velankar (2006b)], but the net effect in the present case appears to be an increase in γ_∞ upon addition of compatibilizer to the B40 blend. The only qualitatively new result as compared to Wang and Velankar (2006b) is the stress dependence of the γ_∞ which has not been studied previously: evidently, the stress dependence of the compatibilized B40-0.1 blend is similar to that of the uncompatibilized B40-0 blend, with γ_∞ being weakly dependent on stress.

In B60 on the other hand, addition of 0.1% compatibilizer has a qualitatively different effect than in B40-0.1. At the highest stress level, γ_∞ of B60-0.1 is comparable to that of B60-0. However, with decreasing stress, γ_∞ for B60-0.1 reduces sharply and becomes much lower as compared to B60-0. Qualitatively, this is attributable to coalescence suppression: with decreasing stress, the drops of B60-0.1 do not coalesce and, hence, at the lower stress levels, these smaller drops are less deformed. Moreover, as will be discussed in Sec. IV B, in the B60-0.1 blends, the interface appears to be at least partially immobilized by the bcp, which is likely to further reduce drop deformation. For both of these reasons, B60-0.1 is expected to have less deformed drops, hence resulting in a lower γ_∞ than B60-0 at low stresses.

IV. DISCUSSION

As mentioned in the Introduction, we have previously documented the effects of compatibilizer in dilute B11 blends with a PIB-in-PDMS morphology. This paper was principally motivated by the observations that (1) the compatibilizer greatly increases the viscosity in 50/50 blends, suggesting that concentrated blends behave differently from dilute blends, and (2) the compatibilizer affects PIB-continuous blends differently than PDMS-continuous blends: it suppresses coalescence if PIB forms the continuous phase, but not if PDMS forms the continuous phase. Therefore, we will first summarize the results of this paper with emphasis on two issues: (1) Concentration effects: How do B40 and B60 blends differ from B11 blends? (2) Phase continuity effects: How do B40 blends differ from B60 blends? The results are summarized in Table I.

It appears from Table I that the rheological effects of compatibilizer on concentrated blends can be summarized as follows: (1) The behavior of concentrated B40 and B60 blends is broadly similar to that of dilute B11 blends with only one noteworthy feature: the effect of compatibilizer on the viscosity, especially terminal complex viscosity, is much larger in the B40 and B60 blends than in B11 blends. The other rheological properties studied (relaxation times, ultimate recovery) do not show such a large difference between the compatibilizer effect in dilute vs concentrated blends. (2) The behavior of B60 blends is similar to that of B40 blends at low compatibilizer levels. However, at high compatibilizer levels, the bcp suppresses coalescence in the B60 blends and, hence, properties such as relaxation time and ultimate recovery are dominated by the effects of coalescence suppression.

In the remainder of this section, we will discuss these two aspects, the high viscosity and the coalescence suppression, in greater detail.

TABLE I. Summary of results.

B40	B60	Remarks and comparison with B11
Dynamic oscillatory moduli and terminal complex viscosity		
Compatibilized blends show two interfacial relaxations (vs. only one for uncompatibilized blends). At high compatibilizer content, the two relaxations merge.		Both B40 and B60 are similar to B11. The additional relaxation may be attributed to interfacial viscoelasticity.
At 0.1% compatibilizer, the terminal relaxation time is much **larger** than in the uncompatilized blend and increases as stress reduces.	At 0.1% compatibilizer, the relaxation time is independent of stress, and much **smaller** than in the uncompatilized blend at low stress.	B40-0.1 is similar to compatibilized B11 blends. The stress dependence of the relaxation time is attributable to coalescence. B60-0.1 is similar to compatibilized B90 blends (unpublished). The stress independence of the relaxation time is attributable to coalescence suppression.
Compatibilizer increases terminal complex viscosity.		Similar to B11, but the compatibilizer effect is far larger in B40 and B60.
Steady shear viscosity, η		
Compatibilizer increases η, especially at low stresses.		Similar to B11, but the compatibilizer effect is larger in B40, and especially in B60.
Ultimate recovery, γ_∞		
Compatibilizer **increases** γ_∞.	Compatibilizer **reduces** γ_∞ at low stresses.	B40 is similar to B11. B60 is attributable to coalescence suppression.

A. Coalescence suppression

Thus far, all of the evidence in this paper supporting coalescence suppression has been rheological. Before discussing coalescence suppression further, it must be confirmed directly. The simplest and most direct test is to leave the sample in a petridish under quiescent conditions. All uncompatibilized blends, and compatibilized blends with PDMS as the majority phase, showed large-scale phase separation visible even to the naked eye after a week. However, compatibilized samples with PIB as the continuous phase maintained their uniformly white appearance for at least two months. Microscopic examination of the B60-0.1 samples also showed only a slight increase in drop size before and after the sample had been kept under quiescent conditions for two months. Thus the conclusion drawn from the rheological experiments appears to be validated: the diblock copolymer can stop coalescence of PDMS drops in PIB, but not of PIB drops in PDMS.

For over a decade it has been accepted that block copolymers can suppress coalescence in droplet-matrix blends [Beck Tan *et al.* (1996); Macosko *et al.* (1996)]. In fact it is now believed that suppression of coalescence is the main reason why block copolymers promote blending of immiscible homopolymers. Yet, this asymmetric coalescence suppression is somewhat puzzling, considering that the block copolymer is not particularly asymmetric ($M_{w,\mathrm{PIB}}=6150$ g/mol and $M_{w,\mathrm{PDMS}}=8000$ g/mol). While asymmetric coalescence has not been well-documented in polymeric systems [however, see Van Hemelrijck *et al.* (2005), discussed below], it is very well-known in oil/water/surfactant systems. There are even well-established rules on which surfactants prevent coalescence of oil drops in water and vice versa. For example, a common rule of thumb, Bancroft's rule, states that a stable water-in-oil emulsion results from a surfactant that has higher solubility in oil than in water, and vice versa.

Two mechanisms have been proposed to explain suppression of coalescence in polymeric systems [Van Puyvelde *et al.* (2001)]. The first is that as two drops approach each other due to the externally applied flow, the block copolymer must be squeezed out of the region between the two drops. This causes a gradient in the bcp concentration and, hence, a Marangoni stress, which inhibits the drainage of the film between the colliding drops, and may also modify the trajectories of drops before they collide [Milner and Xi (1996); Chesters and Bazhlekov (2000); Hu *et al.* (2000)]. If the Marangoni stress is sufficiently large, the portion of the interface bounding the draining film may become nearly-immobilized causing a severe decrease in the coalescence rate. The Marangoni stress mechanism to explain coalescence suppression is based on continuum fluid mechanics and ignores the macromolecular nature of the compatibilizer. In fact, it even applies to oil/water or other small molecule systems with surfactant; the only requirement is that the surfactant reduce the interfacial tension between the immiscible phases.

From a continuum perspective, however, the B40-0.1 and B60-0.1 blends appear to be very similar. The same interfacial tension is expected regardless of which phase forms drops (the asymmetric effects in interfacial tension seen by Ziegler and Wolf (2004) should only occur in blends with very low drop volume fractions). Furthermore, PIB and PDMS have the same viscosity and, hence, the hydrodynamics of drop collision and film drainage should be similar in B40 and B60 blends. Hence, at first glance it appears that the Marangoni stress mechanism cannot explain our asymmetric coalescence suppression. Nevertheless, we cannot altogether rule out the Marangoni stress mechanism: if there is a large difference in solubility and/or diffusivity of the bcp in the two bulk phases, the Marangoni stress mechanism can still predict asymmetric coalescence. In fact, the above-mentioned Bancroft's rule for oil/water systems, which correlates coalescence suppression to the relative solubility of the surfactant between the two phases may be rationalized by the Marangoni stress mechanism [Binks (1998)].

The second mechanism of steric hindrance [Macosko *et al.* (1996)] may also be able to explain coalescence suppression in the present situation. As drops approach each other, the block of the bcp outside the drop must compress, and the force required for this compression corresponds to a repulsive potential between the drops that keeps the drops apart and prevents coalescence. This mechanism applies specifically to polymeric systems and requires that the bcp have a sufficiently high molecular weight [Lyu *et al.* (2002)]. In cases when one block is short and the other is long, asymmetric coalescence suppression is expected. Indeed, Van Hemelrijck *et al.* (2005) noted that a polyisoprene-PDMS diblock with a long polyisoprene block and a short PDMS block could suppress coalescence only when polyisoprene was the continuous phase. As mentioned above, in the present case, the block copolymer is not especially asymmetric. However, from a molecular perspective, the PIB and PDMS homopolymers used here are not at all similar. They have a large difference in molecular weight: $M_w = 1300$ g/mol for PIB vs M_w exceeding 100 000 g/mol for PDMS. Thus, we speculate that the PIB block is highly swollen by the low MW PIB homopolymer and, hence, is an effective steric barrier to coalescence when PIB is the continuous phase. In contrast, we speculate that the PDMS block is not at all swollen and, hence, in a collapsed conformation which cannot hinder coalescence when PDMS is the continuous phase. It must be emphasized that this explanation is only tentative and we do not have direct evidence supporting it. However, unlike

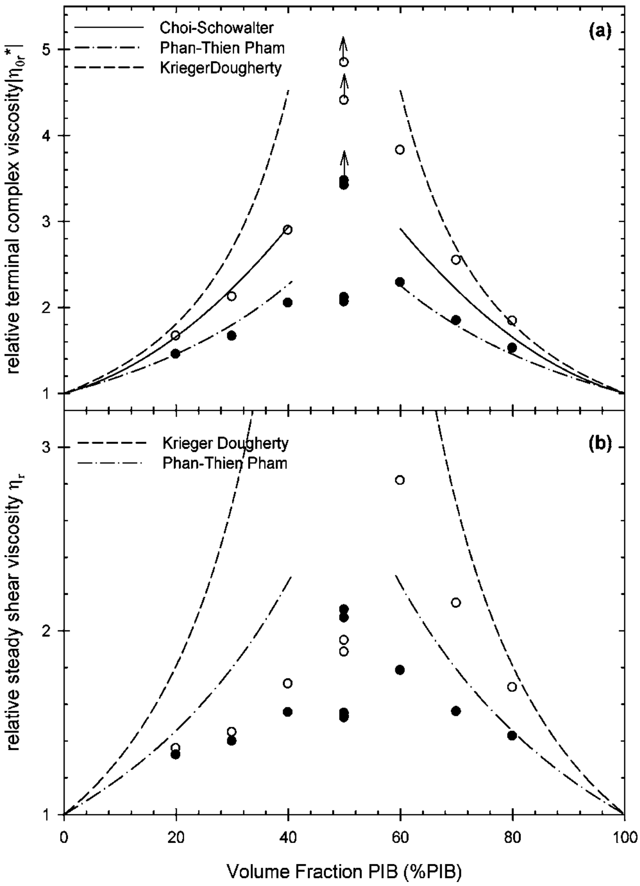

FIG. 8. (a) Relative terminal complex viscosity. (b) Steady shear viscosity at 120 Pa. In both figures, closed symbols are the uncompatibilized blends, and open symbols are blends with 0.1% compatibilizer.

the Marangoni stress mechanism, the steric hindrance mechanism can explain the asymmetry of coalescence suppression without postulating that the block copolymer has different solubility in the two phases.

B. Terminal complex viscosity and steady shear viscosity

The compatibilizer has previously been shown to increase the viscosity of dilute B11 blends [Velankar *et al.* (2004a)]. However, its effect in the concentrated blends studied here, especially B60, is far larger. The experiments of Sec. III A show that at all compatibilizer levels studied here, B40 and B60 blends have a droplet-matrix morphology with the minority phase being the dispersed phase. Thus a morphological change is *not* the cause of this large increase in viscosity and, hence, the quantitative difference between the effect of compatibilizer in dilute vs concentrated blends must be attributed to hydrodynamic interaction between drops. It is, therefore, of interest to examine in detail how the effect of compatibilizer varies with volume fraction of the drops.

We first consider the terminal complex viscosity of uncompatibilized blends. The relative terminal complex viscosities of uncompatibilized blends ranging from 20% PIB to 80% PIB are shown as filled circles in Fig. 8. Taylor's analysis [Taylor (1932)] provides the most basic equation for the viscosity of a surfactant-free emulsion in the low capillary number (or low-frequency) limit when the drops remain undeformed. However, that analysis is restricted to dilute emulsions and is not appropriate here. For concentrated blends, hydrodynamic interactions must be considered. Choi and Schowalter (1975) have extended Taylor's analysis to include hydrodynamic interactions to obtain

$$\eta_{0r} = \frac{\eta_0}{\eta_m} = 1 + \phi_d \frac{5p+2}{2(p+1)} + \phi_d^2 \frac{5(5p+2)^2}{8(p+1)^2}. \tag{7}$$

Ignoring the ϕ_d^2 term in Eq. (7) recovers the Taylor equation [Taylor (1932)]. Note that the η_m in the denominator of Eq. (7) is within 2% of the denominator in Eq. (2) and, hence, Eq. (7) can be compared straightforwardly to the $|\eta_{0r}^*|$ measured experimentally. This comparison is done in Fig. 8(a), and it is evident that Eq. (7) overestimates the viscosity of uncompatibilized blends, as has also been noted previously [Grizzuti *et al.* (2000)]. Much better agreement with the measured $|\eta_{0r}^*|$ is achieved by the equation

$$\eta_{0r}^{2/5}\left(\frac{2\eta_{0r}+5p}{2+5p}\right)^{3/5} = \frac{1}{1-\phi}, \tag{8}$$

which was derived by Phan-Thien and Pham (1997) using an effective medium approach.

Next we turn to compatibilized blends. The relative terminal complex viscosities of all blends with 0.1% compatibilizer are plotted as open circles in Fig. 8(a). Since the terminal complex viscosity is nearly independent of compatibilizer content (Fig. 4), the open circles are very close to the relative terminal complex viscosities at other compatibilizer levels, even as low as 0.01%. These data on the compatibilized blends now better quantify the observation made at the start of this section: the effect of compatibilizer on the viscosity increases with increasing drop concentration. The remainder of this section is devoted to interpreting this observation.

Why does the compatibilizer raise the viscosity of a droplet-matrix blend? A simple mechanism to explain the higher viscosity of compatibilized blends is to postulate that the compatibilizer immobilizes the interface. In the most extreme case of complete immobilization (interface behaves like a solid surface), it is appropriate to compare the viscosity of the blend to that of a suspension of rigid particles. Such a comparison may be made using the Krieger-Dougherty (KD) equation [Larson (1999)]:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m},$$

where ϕ_m is the volume fraction of particles at which the viscosity diverges. In the high shear rate limit (which is appropriate here since the drops are not Brownian), a value of $\phi_{\max}=0.68$ has been suggested [Larson (1999)]. Figure 8(a) shows that the KD equation agrees reasonably well with the relative terminal complex viscosity of blends with PIB as the continuous phase: the viscosity of B80-0.1 is predicted almost exactly, whereas the viscosities of B70-0.1 and B60-0.1 are slightly overpredicted. This conclusion holds even if slightly different values of ϕ_m are used. Thus we conclude that in the terminal region, 0.1% compatibilizer nearly immobilizes the PDMS drops in PIB, causing them to behave nearly like rigid particles. For PDMS-continuous blends on the other hand, $|\eta_{0r}^*|$ lies well below the Krieger-Dougherty prediction (once again, using slightly different values for ϕ_m does not change this), suggesting that the PIB drops in PDMS are only partially immobilized in the terminal region. In summary, our experiments suggest that 0.1% compatibilizer (or, indeed, even 0.01%, since from Fig. 4 the terminal complex viscosity remains the same) is sufficient to nearly immobilize the drop interfaces in PIB-continuous blends, and partly immobilize them in PDMS-continuous blends.

What is the mechanism underlying this complete or partial immobilization of the interface? A possible mechanism is Marangoni stresses as discussed in Sec. III B: the oscillatory strain imposed on the sample can induce gradients in compatibilizer concentration on the interface. The resulting Marangoni stresses reduce the interfacial mobility. The degree of interfacial immobilization depends on the ratio of the Marangoni stresses to the viscous stresses, the Marangoni number [Blawzdziewicz *et al.* (2000)]:

$$\mathrm{Ma} = \frac{\Delta\alpha}{\sigma R} = \frac{\Delta\alpha}{\alpha}\frac{1}{\mathrm{Ca}}, \tag{9}$$

where σ is the characteristic viscous stress experienced by the drop, R is the drop size, and $\Delta\alpha$ is the characteristic change in interfacial tension induced by the viscous stress. In the terminal region of a dynamic oscillatory experiment, stress can be regarded as proportional to frequency and, hence, we can rewrite

$$\mathrm{Ma} = \frac{\Delta\alpha}{|\eta_0^*|\omega\gamma_0 R}, \tag{10}$$

where γ_0 is the amplitude of the oscillatory strain.

The characteristic timescale of an oscillatory flow is ω^{-1}. If the compatibilizer adsorbed on the interface rapidly equilibrates with that dissolved in the bulk, i.e., equilibrates over a time scale much smaller than ω^{-1}, then the interfacial concentration of compatibilizer always remains close to its equilibrium value. In this case, the interfacial tension remains nearly uniform over the surface of the drop during the oscillatory flow. Thus, $\Delta\alpha$ and Ma remain small and there is little immobilization of the interface. In the other extreme, if the compatibilizer is completely insoluble in the bulk, flow-induced changes in compatibilizer concentration on the interface do not equilibrate with the bulk. In this case, a significant $\Delta\alpha$ can be induced by the applied flow, Ma can be large, and significant immobilization can occur.

The greatest extent of interfacial immobilization occurs when $\mathrm{Ma}\rightarrow\infty$. Equations (9) and (10) suggest that the conditions for this are that (1) $\sigma\rightarrow 0$, or in an oscillatory experiment, $\omega\rightarrow 0$, and (2) as $\sigma\rightarrow 0$ or $\omega\rightarrow 0$, $\Delta\alpha$ should remain constant, or at least that $\Delta\alpha$ should decrease less than proportionately to stress/frequency. These conditions correspond to the limit of an incompressible interface—one for which infinitesimal changes in compatibilizer concentration induce finite changes in interfacial tension [Blawzdziewicz *et al.* (1999, 2000)]. Physically, an incompressible interface corresponds to a drop covered by an insoluble compatibilizer in the limit of small applied stress or small oscillatory frequency. In this limit, for dilute emulsions, theory [Oldroyd (1953); Jacobs *et al.* (1999)], numerical simulations [Li and Pozrikidis (1997); Blawzdziewicz *et al.* (2000)], and experiments [Van Hemelrijck *et al.* (2006)] all show that the terminal complex viscosity approaches Einstein's equation for a dilute suspension of rigid particles. This may explain the suspension-like viscosity of B80-0.1.

Yet, all compatibilized blends other than B80-0.1 have terminal complex viscosities lower than that predicted by KD equation; some, such as B70-0.1 are only slightly lower, whereas others, such as B30-0.1 and B40-0.1, are substantially lower. Within the context of interfacial immobilization, two different mechanisms may be proposed to explain these lower-than-suspension viscosities.

The first addresses the much larger deviations from KD equation of the concentrated blends (B60-0.1 and B40-0.1) as compared to the dilute ones (B80-0.1 and B20-0.1). The key idea is that while a single drop with an incompressible interface may behave like a rigid particle, a pair of drops may not. This is because an incompressible interface can still permit “solenoidal” interfacial velocity fields, i.e., fields that have zero divergence [Blawzdziewicz *et al.* (1999); Ramirez *et al.* (2000)]. Thus, drops with an incompressible interface are still not completely immobile like rigid spheres and, in particular, have a weaker hydrodynamic interaction than rigid spheres. Accordingly, even if the interface is incompressible, the viscosity of such an emulsion should be lower than of a rigid particle suspension. This may be the reason why the terminal complex viscosities of blends with larger volume fraction of drops deviate increasingly from the KD equation. Future simulations or theories that model the effect of drop volume fraction on the viscosity of emulsions with incompressible interfaces may be able to test this quantitatively.

The second possibility is that in some blends, Ma is not infinite but has some finite value. This corresponds to a compressible interfacial layer of compatibilizer for which $\Delta\alpha$ decreases proportionately to the stress/frequency. Simulations and theory [Blawzdziewicz *et al.* (2000)] have shown that as Ma decreases from infinity to zero, the viscosity of a dilute emulsion decreases from Einstein’s equation for a dilute suspension to Taylor’s equation for a dilute emulsion. Thus, if different blends have different Ma values, they would also have different viscosities; these viscosities would always be lower than that of a rigid sphere suspension. This explanation is, however, not mechanistic; we are unable to comment on the fundamental reason why Ma would change from one blend to another.

Next we turn to steady shear viscosity. Figure 8(b) shows the steady shear viscosity for all the blends of Fig. 8(a). Only the results at 120 Pa are shown but the discussion applies to all stress levels. As mentioned in Sec. III C, in our uncompatibilized blends, the capillary number increases with increasing shear rate. Hence, under steady shear conditions, the drops are more deformed and oriented along the flow direction causing shear thinning of the blend [Frankel and Acrivos (1970); Choi and Schowalter (1975)]. Accordingly, the η_r values for the uncompatibilized blends in Fig. 8(b) lie well below the Phan-Thien and Pham prediction.

For compatibilized blends under steady shear, the situation is more complex. As explained previously [Li and Pozrikidis (1997); Blawzdziewicz *et al.* (2000); Velankar *et al.* (2004a)], there are now two effects to be considered: drop deformation, which tends to reduce the blend viscosity, and interfacial tension gradients, which tend to increase the viscosity. In the limit of low shear rate (i.e., low Ca), the drops remain nearly spherical and, hence, the drop-deformation effect vanishes. Yet interfacial tension gradients can still exist and partly or fully immobilize the interface and, hence, the compatibilizer always increases the viscosity in the zero shear limit. As stress increases, two changes occur: (1) Marangoni stresses cannot keep the drop interfaces immobile [Ma decreases as per Eq. (9)] and, hence, finite gradients in compatibilizer concentration exist on the drop interfaces, and (2) Ca increases and the drops become increasingly deformed and oriented along the flow direction. Both these effects contribute to shear thinning. The net effect is that compatibilized blends are more shear-thinning than uncompatibilized ones [Li and Pozrikidis (1997); Blawzdziewicz *et al.* (2000)].

This physical picture drawn from theory and simulations [Li and Pozrikidis (1997); Blawzdziewicz *et al.* (2000)] is qualitatively borne out in Figs. 6 and 8(b). It is obvious from Figs. 6 and 8(b) that none of the blends have steady shear viscosities close to the rigid sphere limit. Even in blends such as B80-0.1 or B70-0.1 (not shown), while the compatibilizer can maintain nearly-immobile interfaces at terminally low frequencies, it cannot do so when a stress of 120 Pa is applied. Nevertheless, interfacial tension gradients continue to contribute to the steady shear viscosity. In PIB-continuous blends, this contribution is relatively large; note, for example, the significantly larger viscosity of compatibilized B60 blends as compared to B60-0 (Fig. 6). On the other hand, interfacial tension gradients contribute much less to the viscosity in PDMS-continuous blends; note, for example, that the viscosity of compatibilized B40 blends is only slightly larger than of B40-0 (Fig. 6). Unfortunately, a quantitative comparison of Fig. 6 with the simulations is not possible as specific properties of our compatibilizer needed for comparison to the simulations are unknown.

We have conducted the above discussion entirely in terms of Marangoni stresses (or, correspondingly, an interfacial dilational modulus) as a mechanism of interfacial immobilization. It is important to realize that, while this is probably the simplest explanation for the effect of compatibilizer on the viscosity, other explanations are possible. In particular, it is also possible that the compatibilizer immobilizes the interface by a different mechanism, e.g., by endowing the interface with a shear modulus or a yield stress.

Finally, Figs. 8(a) and 8(b) show the viscosity of B50 blends. The different points refer to different, independently-prepared blends. It is immediately apparent that the viscosities are widely variable, even in the uncompatibilized B50-0 blend. Also, in some runs [points with upward arrows in Fig. 8(a)], the complex viscosities showed no sign of leveling off to a terminal value, at least up to 0.01 rad/s, whereas in other runs a clear terminal plateau was evident. Evidently, the rheology, and presumably the morphology, of blends with equal amounts of PIB and PDMS are highly sensitive to the mixing history, leading to the irreproducibility.

C. Differences between PIB- and PDMS-continuous blends

Summarizing the differences between compatibilized blends with PIB continuous phase (B80, B70, B60) vs those with PDMS continuous phase (B20, B30, B40): (1) compatibilizer suppresses coalescence in PIB-continuous blends; (2) the terminal complex viscosities of compatibilized PIB-continuous blends are close to or slightly lower than those of rigid particle suspensions, whereas terminal complex viscosities of compatibilized PDMS-continuous blends are substantially lower; (3) PDMS-continuous blends undergo shear-thinning at far lower stresses than PIB-continuous blends; (4) the compatibilizer increases the steady-shear viscosity much more in PIB-continuous blends. All these differences may be explained by postulating that the compatibilizer immobilizes the interface much more when PIB is the continuous phase. While it is not clear why the degree of immobilization depends on which phase is continuous, it may make modeling easier. For example, all the four differences above may be modeled by endowing the interface with interfacial viscoelastic properties that depend on which phase is continuous. We reiterate that this is not a mechanistic approach and the fundamental reason why the PIB-continuous blends are immobilized to a greater extent remains unknown.

Finally we note that the *un*compatibilized blends themselves do not show fully symmetric behavior, e.g., both $|\eta_{0r}^*|$ as well as η_r are not symmetric about the 50/50 composition. While the differences between uncompatibilized PIB-continuous blends and uncompatibilized PDMS-continuous blends are not as large as those in the presence of compatibilizer, we are unable to propose a mechanism to explain them.

V. SUMMARY AND CONCLUSIONS

We have conducted a rheological study of immiscible blends of PIB and PDMS compatibilized by a PIB-PDMS diblock copolymer. The purpose of this research was to study the effect of compatibilizer in blends which contained nearly equal amounts of PIB and PDMS. Experiments were performed on blends that contained PIB and PDMS in ratios ranging from 20:80 to 80:20 by volume, although much of the discussion is restricted to blends containing either 40% or 60% PIB and up to 0.1% compatibilizer.

Although the compatibilizer is approximately symmetric, it was found to suppress coalescence of drops when PIB was the continuous phase, but not when PDMS was the continuous phase. In spite of this dramatically asymmetric effect of the compatibilizer, the morphology of blends remains remarkably simple: the majority phase always forms the continuous phase and unusual morphologies are not evident. All rheological effects due to added compatibilizer are qualitatively similar to those of dilute blends studied previously, except that properties that depend on drop size are greatly affected by whether coalescence is suppressed or not. The chief quantitative difference is that the compatibilizer increases the viscosity of the concentrated blends much more than it does dilute blends. This increase in viscosity is attributable to immobilization of the interface due to compatibilizer. In blends with PIB as the continuous phase, the viscosity approaches that expected for a suspension of rigid particles at the same volume fraction, suggesting that the compatibilizer immobilizes the interface almost completely. In blends with PDMS as the continuous phase, the viscosity is lower suggesting only partial immobilization.

ACKNOWLEDGEMENTS

We are grateful to the Laboratory of Applied Rheology at the Katholieke Universiteit Leuven for making the PIB-PMDS diblock copolymer available for this research. We thank Rhodia Silicones and Soltex Chemicals for providing the PDMS and PIB homopolymers respectively. We thank one reviewer for pointing out that an incompressible interface is not a sufficient condition to raise the viscosity of a concentrated emulsion to that of a suspension. This research was supported by a CAREER grant CBET-0448845 from the National Science Foundation, USA, and a grant from the ACS-Petroleum Research Fund.

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