Double Emulsions of Immiscible Polymer Blends Stabilized by Interfacially Active Nanoparticles

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The stability of particle-stabilized double emulsions under flow is of great scientific and technical interest in many fields. In this work, a two-step mixing procedure was adopted to produce double emulsions based on viscous polyisobutylene (PIB)/polydimethylsiloxane (PDMS) blends and a small amount of interfacially active hydrophobic silica nanoparticles were used to stabilize the morphology. The structures of nanoparticle-stabilized double emulsions with varying blend ratios and nanoparticle concentrations were investigated via optical microscopy and rheology technique. It was found that increasing the nanoparticle content effectively facilitated the formation of double emulsion droplets under shear flow and improved their stabilities. Rheology results suggested that these nanoparticle-stabilized double emulsions displayed a slower relaxation dynamics. Decreasing the concentration of dispersed phase was in favor of the generation of more stable double emulsions, possibly due to the higher particle coverage at the interface between two phases. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 4373–4382, 2013

Keywords: double emulsions, nanoparticles, stability, shear flow

Introduction

Multiple emulsions are a kind of complex emulsions in which small emulsions containing smaller emulsion droplets are dispersed as the droplets.[1] The simplest multiple emulsion structure is "double emulsion" or so-called "core-shell structure" as usually found in oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) system, in which one dispersed liquid contains one or more inner droplets which are further dispersed in another liquid. Multiple emulsions have been studied extensively since William Seifriz[2] first discovered the phase inversion of ordinary emulsions in 1925. Multiple emulsions have great potential in the fields of paint, pharmaceutical, food, cosmetics, etc. For example, in pharmaceutical industry, the release rate of active ingredients contained in multiple emulsions could be controlled to enhance their treatment effect.[3,4] In the food industry, multiple emulsions could be used to improve the solubility of active ingredients or materials, and to encapsulate or protect active food components.[5]

Unfortunately, the special structures formed in multiple emulsions are inherent and thermodynamically unstable. This structural instability is mainly caused by the excess free energy associated with the significant increase in the interface area of these systems.[6] Spontaneous coalescence and demulsification process usually occur during the preparation, storage, and use process of multiple emulsions. Thus, special caution is required in manipulating these systems in practical applications to avoid the destruction in morphology. The addition of a third component (such as surfactant, emulsifier, and biological macromolecule) with interfacial activity has been proved to be beneficial to the reduction in the interfacial free energy and the structure stabilization of W/O/W or O/W/O systems.[7] Lots of efforts have been dedicated in illuminating their stabilization mechanisms and efficiencies under various conditions.

Besides various kinds of molecular surfactants or emulsifiers, the use of inorganic solid particles as morphological stabilizers for simple oil-water emulsions with low viscosities has also been a long history since the pioneer works of Ramsden[8] and Pickering[9] in the early 1900s. However, differences between colloidal particles and surfactant molecules in stabilizing emulsion and foam systems exists, which seems to stem from the absence of solubilization and the strong residence tendency of particles at interfaces.[10] The wetting angle, concentration, and size of solid particles are known as key factors in controlling the stability. Recently, there is a rejuvenation of interest in using solid particles like silica or clay differing in hydrophobicity as emulsifiers for the stabilization of multiple emulsions consisting of low molecular weight liquids possibly due to the continuous and considerable development of nanotechnology.[11] Some of the most representative works have been carried out by Binks et al.[12–15] and other groups.[16,17] In their studies, they concentrated on the effect of nanoparticles (with different contact angles and shapes) and properties of liquids (such as surface tension and temperature) on the inversion, rheology, and deposition characteristics of these systems.

However, oil-water systems usually possess low viscosities and rapid kinetic process. This makes it very difficult to

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reveal the structural evolution dynamics and the underlying mechanisms in these systems under flow even in the presence of solid particles. Polymer blends with higher viscosities have a relative slower kinetic process and are expected to be suitable model systems for investigating the formation mechanism and structural stability of multiple emulsions in the presence of various kinds of solid particles. Although charge interactions which usually exist in oil/water aqueous systems is absent or relative weak in common polymer blends, it is believed that revealing the morphology of particle-stabilized double emulsion based on polymer blends is undoubtedly beneficial to a better understanding of the role of other properties of nanoparticles on the morphology of double emulsions. The formation of double emulsions or core-shell structures in polymer blends with high viscosity is not new. It usually involves the addition of a third nonreactive[18–21] or reactive[22] component to form ternary blends or the utilization of special mixing protocols[23] to induce phase inversion. However, using solid nanoparticles to promote the formation of double emulsions in viscous polymer blends has not yet been reported, although recently different kinds of inorganic particles have been used to control the size and stability of desired morphology.[24–26] It is generally recognized that the morphological stabilization mechanism of particle-filled polymer blends is related with the decrease in interfacial tension, the formation of rigid particle layer at the interface, the prohibited film drainage between droplets, and the enhanced viscoelasticity of components.[26–30]

In this work, blends of polyisobutylene (PIB) and polydimethylsiloxane (PDMS) were used as model system and hydrophobic fumed silica nanoparticles were used as an interfacial agent to study the effect of nanoparticles on the formation and stability of viscous double emulsions under simple shear flow. The system is chosen based primary on two reasons. On one hand, PIB and PDMS can form simple emulsions with moderate viscosity and interfacial tension at room temperature. This blend allows long-term rheological experiments without fear of thermal degradation. On the other hand, the results of Moldenaers et al.,[27,31] Velankar et al.[32] and ours[33–36] have showed that hydrophobic particles are mainly trapped at the interface of PIB/PDMS blends and can change the morphology-rheology relationship of blends greatly. Suppressed coalescence,[31] expansion in morphological hysteresis zone[36] and gel-like behavior[32] have been reported due to the absorbed solid hydrophobic particles at the interface. In this work, the possibility of using hydrophobic fumed silica nanoparticles as interfacial agent to promote the formation and stability of double emulsions based on PIB/PDMS blends under simple shear flow was examined. The influence of nanoparticle concentration and component ratio of polymers on the stability of double emulsions structure under flow was explored.

Experimental Section

Materials and sample preparation

The blends consisted of PDMS from Aldrich and PIB from Daelim Co. Both of them are near-Newtonian liquids at 25°C. The preparation of samples, microscopy, and rheological experiments were all conducted at room temperature. The properties of polymers are listed in Table 1. The interfacial tension between PIB and PDMS at 25°C is 1.92 mN/m as reported by our previous studies.[34,36] Dimethyldichlorosilane (DMDCS)-treated fumed silica nanoparticles (Aerosil R974, Degussa) with a primary diameter of 12 nm were used as hydrophobic filler. These fumed silica nanoparticles were actually aggregates with highly fractal structure (Figure 1). A very small amount of nanoparticles (i.e., 0.2, 0.5, and 0.8 wt%) were added into blends. These SiO_2 nanoparticles were dried at 120°C for 6 h prior to use.

PIB/PDMS blends with three different compositions including 30/70, 20/80, and 10/90 were investigated. PDMS was always the continuous phase for its weight fraction dominating in this experiment. Samples were prepared by hand-mixing a certain amount of fillers and polymers with a spatula in a beaker, and then degassed in vacuum to remove the air trapped. In order to prepare blends with double emulsion structure, a two-step blending sequence similar to that adopted by Velankar et al.[19] was chosen, as shown in Figure 2. Samples were designed as $B\varphi_{\mathrm{PIB}}$-w_{R974}, where φ_{PIB} is the mass fraction of PIB and w_{R974} is the weight percentage (%) of R974 nanoparticles. In the first step, PDMS, PIB, and R974 were blended simultaneously to prepare PDMS/PIB blends stabilized by R974 (i.e. B70–0.2). A mixing time of about 20 min was required to ensure the uniform dispersion of PDMS in PIB. R974 nanoparticles used in this step were supposed to locate at the interface of blends. It is because that R972 nanoparticles, which have a similar primary particle size (16 nm) and are also treated with DMDCS, were found to locate at the interface of PIB and PDMS.[27,31] Then, a mixture of PDMS and R974, denoted as B0–0.2, was prepared as the matrix phase for double emulsions. Thus, fillers were designed to stabilize both the inner and external interface of double emulsions. Finally, B70–0.2 was blended with B0–0.2 according to the certain proportion. For example, 5.01 g B70–0.2 ($PIB:PDMS:SiO_2 = 3.5$ g:1.5 g:0.01 g = 70:30:2) was blended with 6.6834 g B0–0.2 ($PDMS:SiO_2 = 6.67$ g: 0.0134 g = 100:2). The final blend was denoted as B30–0.2. The second blending step should involve gentle blending to avoid the leakage of inner PDMS droplets during mixing.

Morphology characterization

The morphology development of PIB/PDMS/R974 blends during shearing were tracked with a Linkam CSS-450 Cambridge Shearing System (Linkam Scientific Instruments, UK) mounted on an Olympus microscope equipped with long working distance objectives and a PixeLINK CCD camera. The temperature was controlled at 25°C. Morphologies of samples before and after shearing were recorded. The morphology evolution during shearing was collected as well. Due to the difficulty in the size statistics of dispersed droplets with an obviously uneven distribution the morphology of

Table 1. Material Parameters at 25°C

Materials	Zero Shear Viscosity (Pa·S)	Density (kg·m^{-3})	Refractive Index	Supplier
PDMS	95.6	963	1.405	Aldrich, America
PIB	77.9	701	1.499	Daelim Co, Ltd, Korea

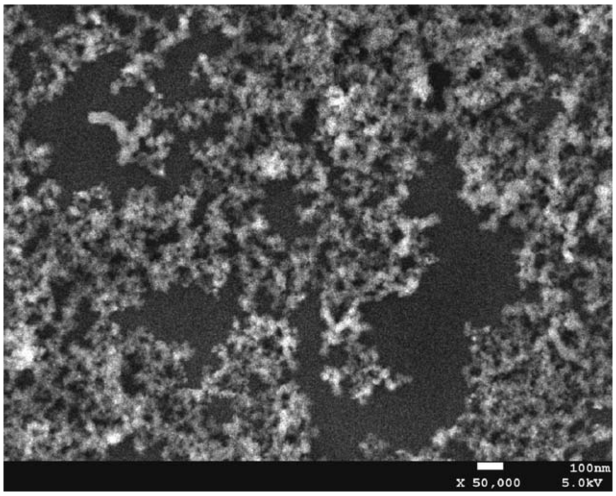

Figure 1. SEM of fumed silica nanoparticles (Aerosil R974, Degussa) used in this study.

multiple emulsions was discussed only qualitatively in this work.

Rheological characterization

Rheological experiments were performed with a strain-controlled rotational rheometer (ARES, TA Instrument). The instrument was equipped with a cone-plate geometry (diameter 25 mm, cone angle 0.099 radians) to ensure a constant shear rate and identical shear history through the sample. A Peltier cell was used to maintain the experiment temperature at 25°C. Dynamic frequency sweep of prepared samples were conducted at a strain of 10%, and then followed the steady shear for 2000 or 4000 strain units at different shear rates. Dynamic frequency sweep tests were also performed within an angular frequency range of 100–0.02 rad/s after shearing immediately to determine the morphology of blend rheologically. The relaxation time spectra of samples were calculated by the commercial Orchestrator software. It should be noted that the droplet size may be comparable to the geometry gap in some cases, such as in blends as prepared and in blends with a high volume fraction of dispersed phase. Thus the rheological data were only compared qualitatively in these cases. Also, the unreliable data at low frequencies were cut off in systems with low moduli according to the minimum measurable torque criterion.

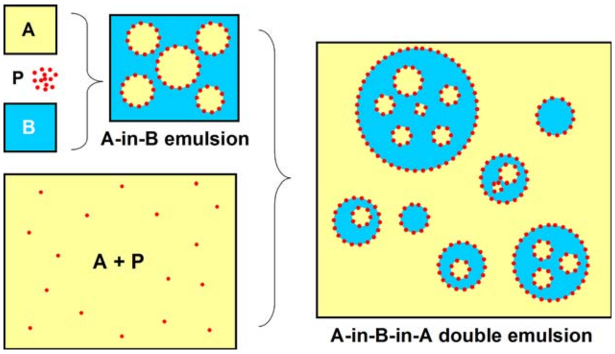

Figure 2. Generation of particle-stabilized double emulsion based on viscous PDMS (A) and PIB (B) via a two-step blending procedure similar to that adopted by Velankar et al.[19]

P stands for hydrophobic silica nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

Results and Discussion

Formation of double emulsion structure

Coalescence or flocculation can happen during the preparation, degassing, and storage of multiple emulsions. In order to study the effect of nanoparticles on the formation of double emulsions, the morphology of blends as prepared after the mixing sequence and degasification were recorded. The morphologies of B30–0, B30–0.2, B30–0.5, and B30–0.8 blends as prepared are showed in Figure 3. The size distribution of dispersed phase is broad after the gentle stirring in the second blending step, especially for the B30–0 sample. As shown in Figure 3a, large layer-like PIB domains containing small PDMS droplets with a diameter about 2–80 μm is formed during the degassing time. There is scarcely any spherical double-emulsion structure existed in the blend. Thus, the two-step blending procedure did not produce stable and well-defined double emulsions in the unfilled blends.

However, when only 0.2 wt% R974 nanoparticles are filled into blends (Figure 3b), double emulsion droplets with diameter about 100–200 μm which dispersed in the whole field of view can be identified. This means that the formation of double emulsion structure is promoted. In other words, compared with sample B30–0, coalescence of droplets is hindered or slow down in the presence of R974 nanoparticles, just like the case in simple blends filled with colloidal particles.[27] The presence of finer inner droplets in double emulsions increases the total interface area of blends and make them appear darker compared with those unfilled ones due to the more noticeable scattering and diffusion of light in these samples. Besides double emulsion droplets, pure PIB droplets with diameter about 30 μm could also be found in B30–0.2 sample and they appeared lighter under microscope. Similar particle-stabilized double emulsions also present in the blends of B30–0.5 and B30–0.8 (Figures 3c, d). When 0.8 wt% nanoparticles are added (Figure 3d), the size of inner PDMS droplets becomes so small that these inner droplets can not be distinguished from each other clearly. Thus, these double emulsion droplets appear the darkest under microscope. Some researchers[37,38] indicated that the magnitude of reduction in the size and uniformity of dispersed phase in polymer blends increased with the content of fillers. Here, the incorporation of R974 nanoparticles increase the retention of the double emulsion structure and diminish the size of their inner droplets. However, the overall degree of droplet dispersion does not increase apparently with increasing nanoparticle content in double emulsion droplets (as shown in Figures 3c,d). The reason for this may be that the highest nanoparticle content used here is only 0.8 wt%, which is much small than the nanoparticle content (usually 3–5 wt%) used in previous studies.[37,38] Another possible reason may be that these double emulsion droplets became more difficult to be destroyed during the second mixing procedure due to the presence of inner PDMS droplets.

Figure 4 shows the storage modulus G' of these samples as prepared. The storage modulus of B30–0 sample shows a wide plateau in low frequencies. It is well-known that the presence of deformable droplets in immiscible blends usually increases their elasticity in low frequencies due to the form

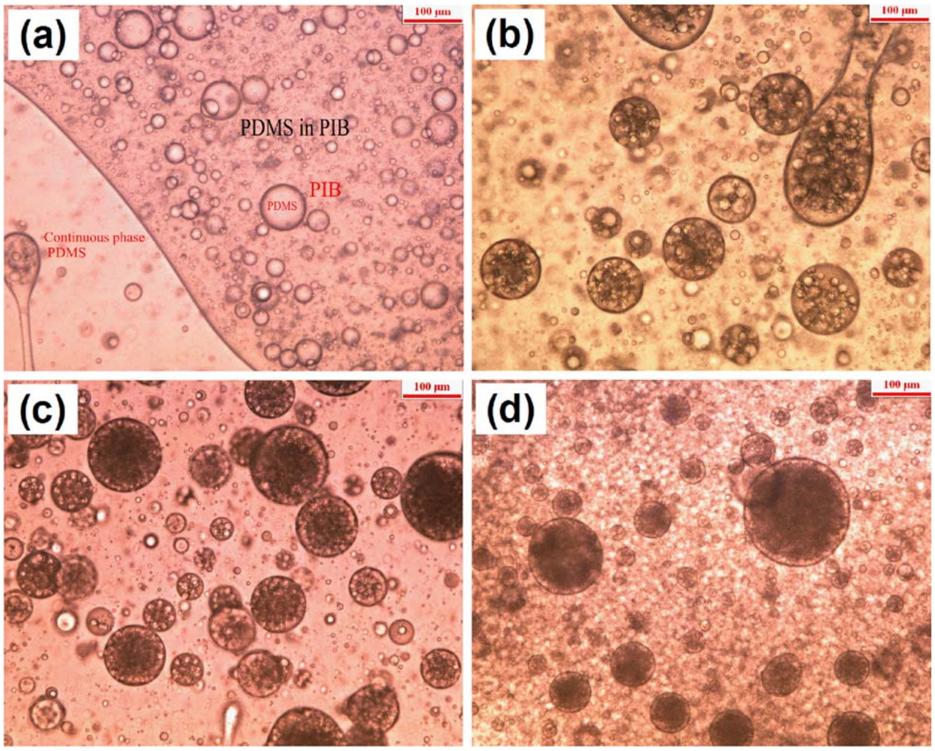

Figure 3. Optical micrographs of as-prepared PIB/PDMS/R974 blends with different nanoparticle contents: (a) B30–0; (b) B30–0.2; (c) B30–0.5; (d) B30–0.8.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

relaxation of droplets.[39,40] As a result, a "shoulder" usually appears in the $G' \sim \omega$ curve. The wide modulus plateau for the as-prepared B30–0 sample can be ascribed to the presence of large layer-like PIB domains possessing long relaxation times (λ) (Figure 3a). Within the accessible frequency range of our rheometer, only a part of the shoulder is displayed. This point is more evident in the weighted relaxation time spectra (namely the $H(\lambda)\cdot\lambda \sim \lambda$ profile) provided in Figure 5. The relaxation time spectrum for as-prepared B30–0 sample rises abruptly at $\lambda > 100$ s. The characteristic relaxation time of a droplet with radius R can be calculated as[41]

$$\lambda = \frac{R\eta_m}{\alpha} \frac{(19p+16)(2p+3)}{40(p+1)} \tag{1}$$

where p is the viscosity ratio, α is the interfacial tension, and η_m is the viscosity of matrix phase. According to Eq. 1, the

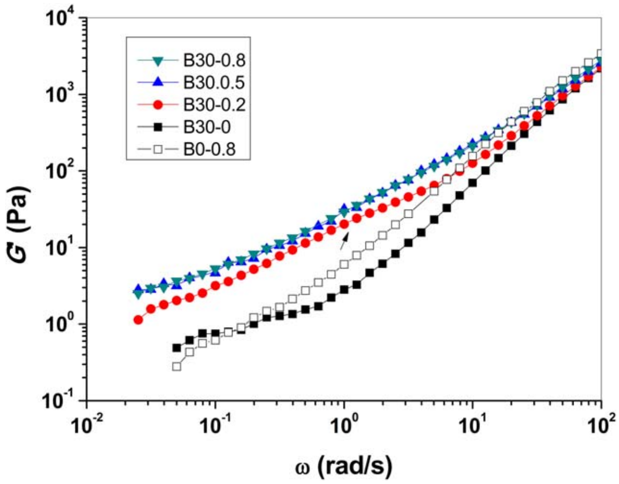

Figure 4. Storage modulus *G*' of as-prepared PIB/PDMS/R974 blends with different nanoparticle contents.

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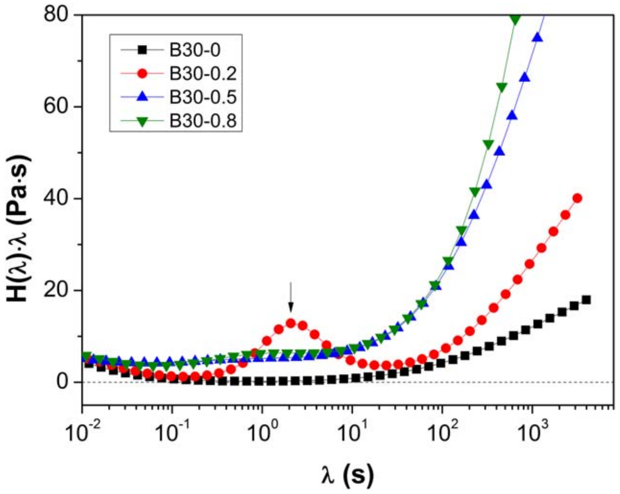

Figure 5. Weighted relaxation time spectra of as-prepared PIB/PDMS/R974 blends with different nanoparticle loadings.

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roughly estimated characteristic size for the structure with $\lambda>100$ s in unfilled PIB/PDMS blends should exceed 800 μm at least in one dimension. It is interesting that the relaxation time spectrum does not display noticeable peak coming from the interfacial relaxation of inner PDMS droplets which should be located around 1–5 s according to their droplet size presented in Figure 3a and Eq. 1. A possible reason for this phenomenon may be that the effect of relaxation of inner droplets on the rheology properties is concealed by that of the large outer layer.

The $G' \sim \omega$ curves of blends filled with R974 nanoparticles are different to that of pure blend. Higher storage modulus in their low frequency regions should be the result of increased interfacial area rather than that of R974 nanoparticles added. It is because PDMS filled with 0.8 wt% nanoparticles (denoted as B0–0.8 in Figure 4) does not exhibit any noticeable enhancement of modulus in low frequencies (PIB filled with 0.8 wt% nanoparticles shows the similar rheology behavior). There is a distinct "shoulder" around 1 rad/s (indicated by the arrow in Figure 4) and elasticity enhancement at lower frequencies on the modulus curve of B30–0.2 sample. Accordingly, the relaxation time spectrum of B30–0.2 sample displays a peak around 2 s and a less noticeable upturn at $\lambda>100$ s. These results suggest that small droplets together with larger phase structure were generated in this sample when only a small amount of nanoparticles was added. The small droplet size with a characteristic time of 2 s is calculated to be 40 μm according to Eq. 1 if a constant interfacial tension is used, which is close to the size of pure PIB droplets in Figure 3b.

The $G' \sim \omega$ curves of B30–0.5 and B30–0.8 are slightly higher than that of B30–0.2 and they are nearly overlapped. Thus, the rheology data together with the optical micrographs all suggest that the difference between morphologies of B30–0.5 and B30–0.8 is small. No distinct shoulder can be identified in the modulus curves of these two samples. These two modulus curves exhibit an approximate power law behavior with a decreased slope in the low frequency region, indicating that the relaxation time of structures presented in these samples possesses a high polydispersity.[42] Accordingly, their relaxation time spectra demonstrate a much pronounced upturn in the long time region but a weak relaxation time peak around 1 s, as shown in Figure 5. Usually, the high polydispersity in the relaxation time of immiscible polymer blends comes from the wide distribution in phase size.[42] However, in this work, this high polydispersity in the relaxation time may also stem from the complex structure of multiple emulsion droplets[43,44] and the preferential location of R974 nanoparticles at the interface of PIB/PDMS blends which might slow down the interfacial dynamics.[31] For these reasons, it is difficult to extract the complicated structure features of nanoparticle-stabilized double emulsions from their rheological data using available modified Palierne model originally derived for so-called sphere-in-sphere morphology[43] or emulsion-in-emulsion structures.[44]

Stability of double emulsions under flow

The structure stability of double emulsions against flow is vital during the preparation or in use and should be paid close attention. Figure 6 shows the morphologies of PIB/PDMS blends after shearing upon the addition of different contents of R974 nanoparticles. The samples were sheared at 0.2 s^{-1} and 0.5 s^{-1} for 10,000 s and 4000 s respectively in order to ensure a same strain of 2000 units.

The steady morphology of immiscible polymer blends in the flow is determined by the dynamic equilibrium of breakup and coalescence processes.[45] Figure 6a shows that a well-distribution of mainly pure PIB droplets emerged in the B30–0 sample after shearing at 0.2 s^{-1} for 10,000 s. The diameter of these droplets ranges from 40 to 80 μm. This means that the breakup process was dominated when the huge layer structure of PIB phase was sheared even at a low shear rate of 0.2 s^{-1}. Most of the PDMS phase which originally dispersed as inner droplets in the huge PIB phase leaked out and merged with the PDMS matrix under flow. Figure 7a shows the storage modulus of B30–0 samples experienced different flow histories. A "shoulder" appears after shearing at 0.2 s^{-1} instead of the plateau for as-prepared sample (Figure 4), implying the formation of droplets with a relaxation time about 9 s as deduced from the relaxation time spectrum in Figure 8a. After shearing at 0.5 s^{-1} for 4000 s, a much finer morphology of pure droplets presents (Figure 6b) and the shoulder in Figure 7a moves to a higher frequency (corresponding to the relaxation time peak around 2 s in Figure 8b). These results clearly embody the refinement and homogenization effect of shear flow on the droplet size. The shift both in the modulus shoulder and relaxation time peak, on the other side, reflects the unstable nature of the as-prepared morphology against shear flow.

Morphologies of nanoparticle-filled samples are showed in Figures 6c–h. For the B30–0.2 sample (Figure 6c), lots of large double emulsion droplets with diameter about 60–100 μm survive after shearing at 0.2 s^{-1}. The shoulder in the $G' \sim \omega$ curve of B30–0.2 shifts to a higher frequency and becomes more noticeable (Figure 7b). In the meantime, the upturn in the right side of the relaxation time spectrum of as-prepared sample (Figure 5) declines in Figure 8a. However, a modest plateau still presents in the long relaxation time region of B30–0.2, suggesting the retention of double emulsion structure after shearing. Nanoparticle-stabilized samples experience stronger shear force at 0.5 s^{-1}. Figure 6d shows that the application of a higher shear rate of 0.5 s^{-1} destroys most of the double emulsion droplets in B30–0.2. The storage modulus curves of B30–0.2 after shearing at 0.2 s^{-1} and 0.5 s^{-1} for the same strain are almost identical at a glance and can not manifest the discrepancy in the destruction of samples under different shear strengths. However, noticeable differences can still be found in their relaxation time spectra. First, the relaxation time spectrum of B30–0.2 with $\lambda>300$ s declines after shearing at 0.5 s^{-1} than that after shearing at 0.2 s^{-1}, suggesting the decrease of double emulsion droplets. Second, at the same time, a new relaxation time peak around 45 s appears in the spectrum of B30–0.2 after shearing at 0.5 s^{-1} (Figure 8b), corresponding to the formation of new structure after the destroying of double emulsion droplets. Thus, the relaxation time spectrum is more sensitive than the modulus curve in revealing the change in the morphology of double emulsions under flow.

As 0.5 wt% of nanoparticles are added into the blends, the retention of double emulsion droplets under shear increases obviously (Figures 6e–f). Meanwhile, the difference between the storage modulus curves of B30–0.5 before and after shearing become smaller compared with that of B30–0.2, as shown in Figure 7c. However, the improvement in the brightness of these double emulsion droplets after shearing

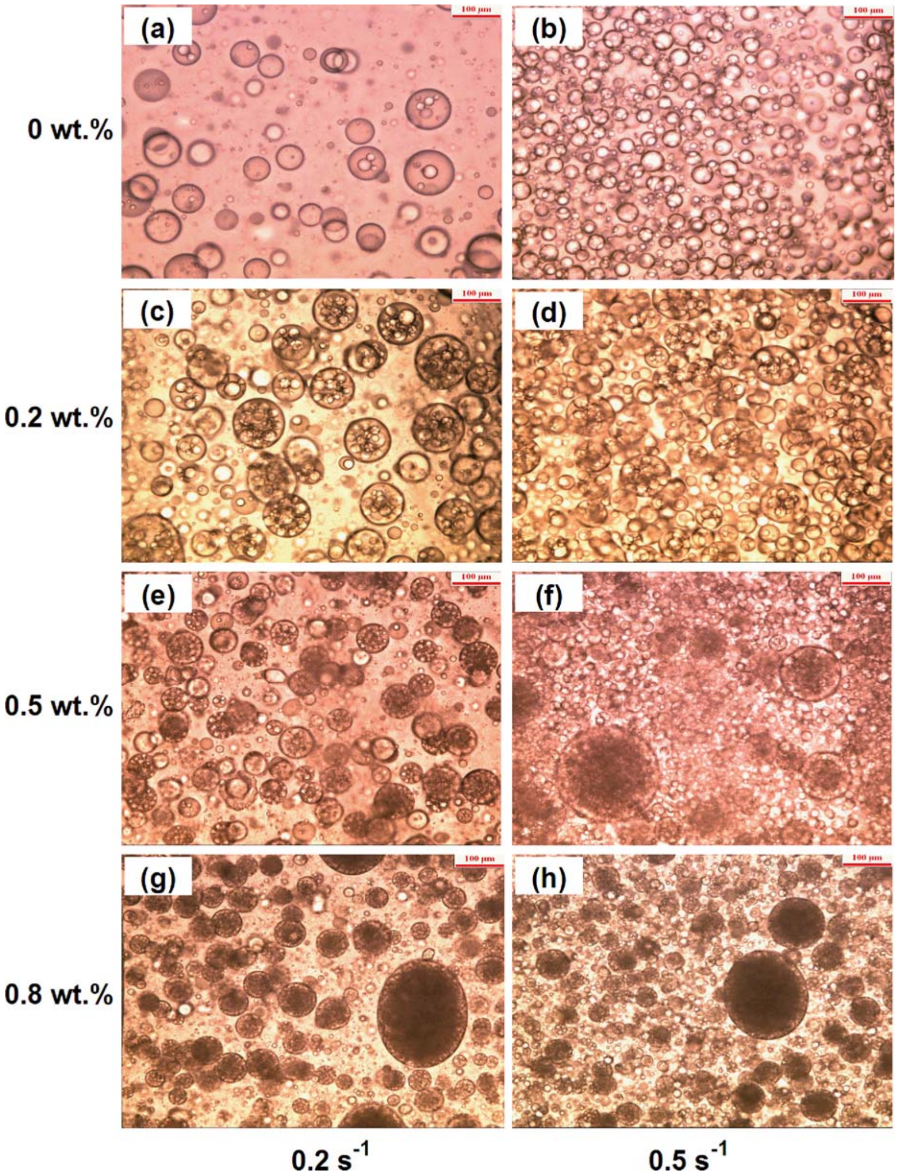

Figure 6. Morphologies of PIB/PDMS/R974 blends with different nanoparticle contents after shearing: (a,b) B30–0; (c,d) B30–0.2; (e,f) B30–0.5; (g,h) B30–0.8.

The images in the left column were taken after shearing at 0.2 s^{-1} for 10,000 s. The images in the right column were taken after shearing at 0.5 s^{-1} for 4000 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

suggests that some inner PDMS droplets still coalesce under flow. Figure 8a shows that the relaxation time spectrum of B30–0.5 after shearing at 0.2 s^{-1} does not show an upturn in the long time region as observed in that of as-prepared sample. In stead, it displays a weak peak at 2 s and a much wide peak at 52 s. Similar to B30–0.2, shearing at 0.5 s^{-1} destroys part of the double emulsions and decreases the overall droplet size of the sample. But there are still some double emulsions with diameter larger than 100 μm existing in the sample (Figure 6f).

When 0.8 wt% nanoparticles are added, the change in the morphology and modulus of the B30–0.8 sample under flow displays a similar tendency to that of B30–0.5 but with a less magnitude. The retentions of double emulsions after shearing at 0.2 s^{-1} and 0.5 s^{-1} both improve significantly. Compared to the as-prepared sample, the relaxation time spectrum of B30–0.8 displays a less profound upturn in the long time region after shearing at 0.2 s^{-1}. This upturn becomes subtle at 0.5 s^{-1}.

Figures 6 and 7 demonstrate that the sensitivity of morphology against shearing declines progressively with increasing nanoparticle loading. Vermant et al.[27] showed that the hydrophobic silica particles decreased the shear rate dependence of microstructure in simple emulsion of PIB/PDMS blends within a certain shear range. The same phenomenon is found in these double emulsions stabilized by silica nanoparticles in this work.

Above results suggest that the incorporation of small amount of interfacially active nanoparticles can not only promote the formation of double emulsions prepared via the two-step mixing procedure but also can effectively improve their morphology stability under shear flow. The improved stability of double emulsions likely comes from the trapping of R974 nanoparticles at the interface between PIB and

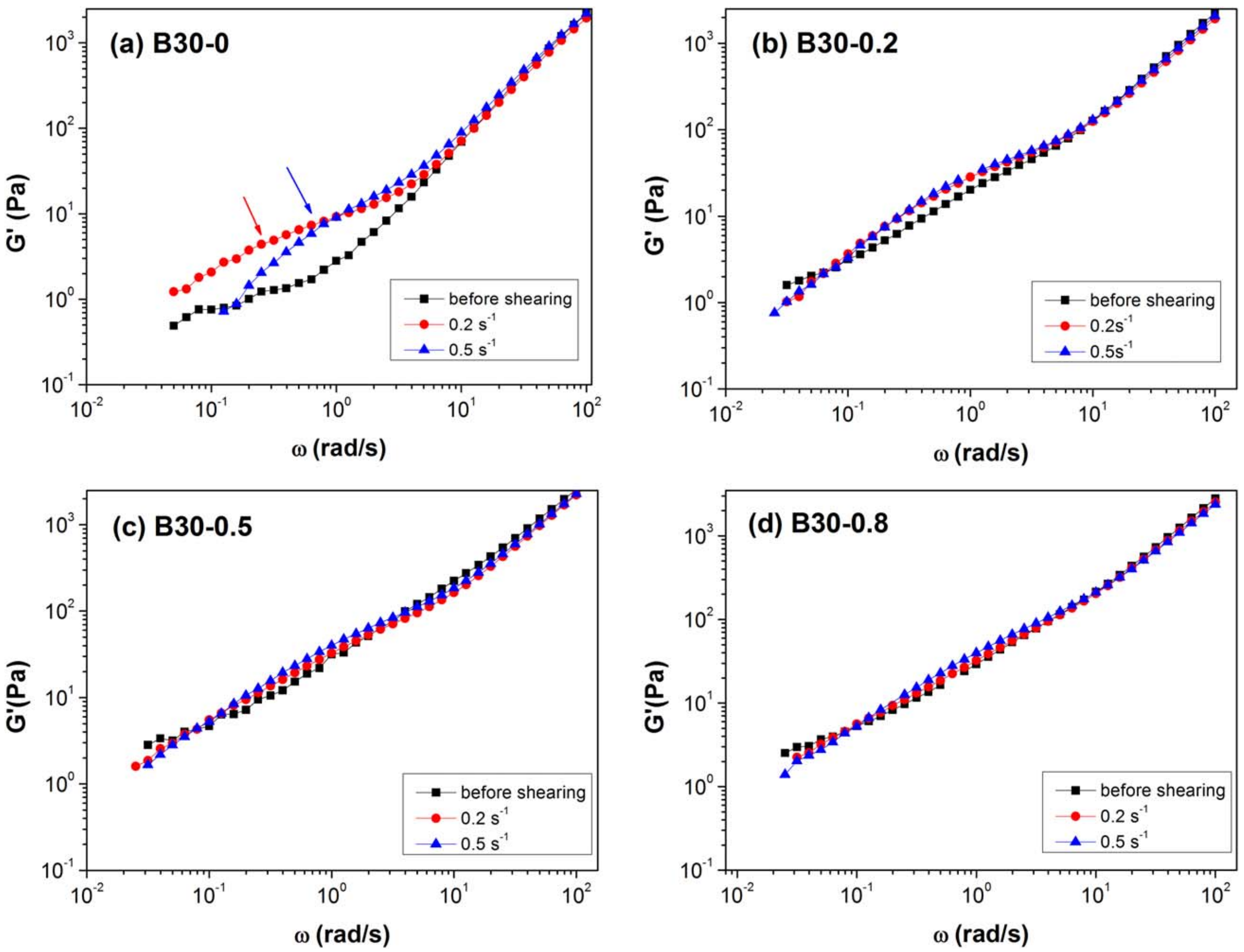

Figure 7. Storage modulus *G*' of PIB/PDMS/R974 blends with different contents of SiO_2 nanoparticles before and after shearing: (a) B30–0; (b) B30–0.2; (c) B30–0.5; (d) B30–0.8.

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PDMS phase which act as a physical barrier at the interface[27,28] and restrain the coalescence not only between inner PDMS droplets but also between double emulsions themselves.

It should be pointed out that the improved morphological stability of double emulsion structure upon the addition of hydrophobic R974 nanoparticles depends not only on the shear rate but also on the strain. As mentioned before, the

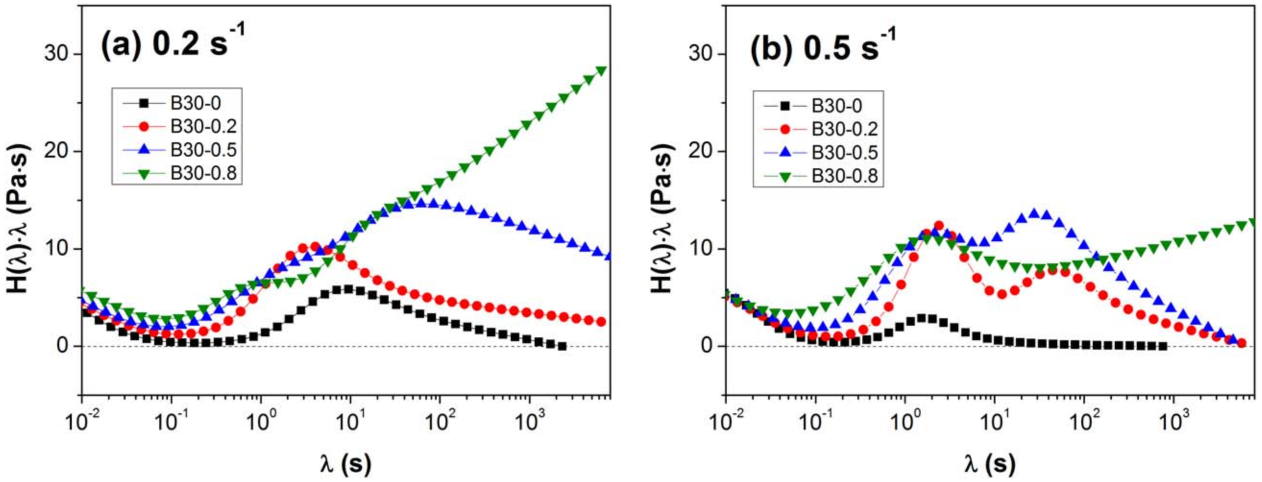

Figure 8. Weighted relaxation time spectra of PIB/PDMS/R974 blends after (a) shearing at 0.2 s^{-1} for 10,000 s and (b) shearing at 0.5 s^{-1} for 4000 s.

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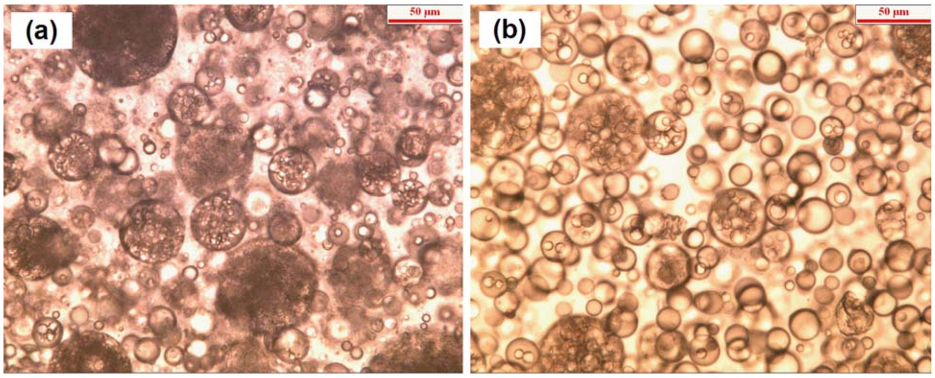

Figure 9. Morphology comparison of B30–0.8 samples after shearing at 0.5 s^{-1} for different times: (a) 4000 s; (b) 8000 s.

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stability of double emulsions in the B30–0.8 sample is still good after shearing at 0.5 s^{-1} for 4000 s. However, when the shearing time at 0.5 s^{-1} is prolonged to 8000 s (Figure 9), further destruction of double emulsions can be observed. The increased brightness of double emulsions indicates the occurrence of coalescence between the inner PDMS droplets contained. Some pure PIB droplets are also presented in the sample after shearing for a longer time. It is interesting to note that at the same time, the size of particle-filled double emulsions, namely, the outer diameter, does not display a noticeable difference after shearing. This result suggests an asymmetric effect of nanoparticles in coalescence suppression as reported in simple emulsions[27] which might be related with the contact angle of nanoparticles trapped at the interfaces. Thus, in order to obtain a better stabilization effect on double emulsions under flow, different nanoparticles with finely tuned wetting angles should be chosen during different mixing steps. However, as long as the shear strain is controlled below a certain value, the double emulsions stabilized by a high content of R974 nanoparticles would be stable.

Stability of double emulsions with different compositions

The shape, size, and size distribution of dispersed phase in immiscible polymer blends are closely linked to its concentration.[46,47] Decreasing the concentration of dispersed phase is likely to decrease the collision probability of droplets during mixing and leads to a slower coalescence rate.[48] Thus, smaller domain size is usually produced in blends with a low weight fraction of dispersed phase. Figures 10a and c

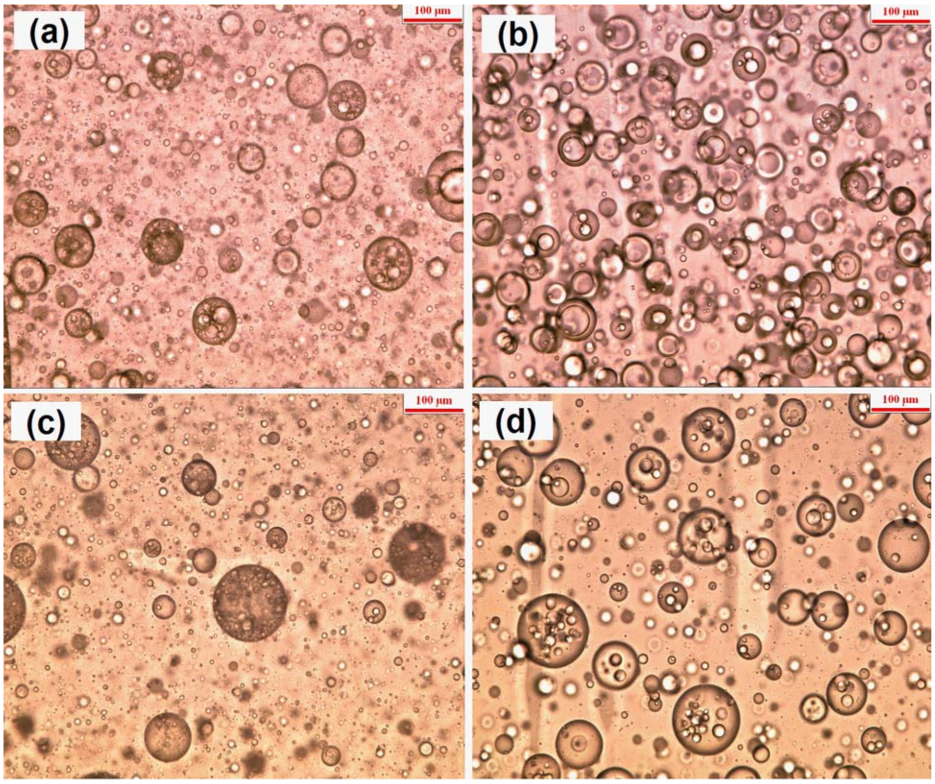

Figure 10. Morphologies of nanoparticle-free samples: (a) B20–0 as prepared; (b) B20–0 after shearing at 0.2 s^{-1} for 10,000 s; (c) B10–0 as prepared; (d) B10–0 after shearing at 0.2 s^{-1} for 10,000 s.

The scale bars denote 100 µm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

show the morphologies of B20–0 and B10–0 prepared via the same two-step mixing procedure. Unlike the layered morphology of B30–0 observed previously, B20–0 and B10–0 form mainly double emulsion droplets. Thus, the decrease in the volume fraction of PIB phase facilitates the formation of double emulsion droplets. It is understandable since a lower PIB concentration is unfavorable to the coalescence of double emulsion droplets during degassing and consequently unfavorable to the formation of layered structure with large size. These double emulsions which formed in blends with a lower composition do not possess a good stability under flow. As shown in Figures 10b and d, most of them are destroyed after shearing at 0.2 s^{-1} for 10,000 s.

In order to stabilize the structure of double emulsions under flow 0.8 wt% of nanoparticles were added into these samples. Figures 11a and c show that more double emulsions were generated in B20–0.8 and B10–0.8 samples as expected. Moreover, after shearing at a higher rate of 0.5 s^{-1} for a larger strain of 4000 units, most of the double emulsions retained in these nanoparticle-filled samples. The superior stability of nanoparticle-stabilized double emulsions in the B20–0.8 and B10–0.8 under flow than that of B30–0.8 (Figure 9b) should be attributed to the change in the interface area of samples. As the weight fraction of PIB phase decreases, less interfacial area is created in these samples and the nanoparticle coverage at the interface should be higher than that of the B30 sample. As a result, a strong steric hindrance of nanoparticles[28] or greatly changed interfacial rheology[31] is expected and will contribute for a better stability of double emulsion formed.

Conclusions

The effect of interfacially active fumed silica nanoparticles on the formation and the stability of multiple emulsions consisting of Newtonian-like PIB/PDMS blends prepared via a two-step mixing procedure were explored qualitatively. The formation of double emulsions in PIB/PDMS blends is facilitated with the loading of only a very small amount (as less as 0.2 wt%) of hydrophobic nanoparticles. The existence of hydrophobic nanoparticles is in favor of promoting the stability of double emulsions under shear flow although the samples still present a strain-dependent stability. Nanoparticles with different wetting angles may be required in order to stabilize both the inner and outer interfaces of double emulsions under flow. The relaxation time spectrum is more sensitive than the modulus curve in characterizing the destruction of nanoparticle-stabilized double emulsions under flow. Decreasing the composition of minor phase is favorable to the formation of double emulsions. However, the addition of interfacially active nanoparticles is yet required in order to maintain the morphology under shear flow. To sum up, stable double emulsion can be prepared from viscous PIB/PDMS blends via the two-step mixing procedure by optimizing the component composition, nanoparticle concentration and flow history. However, in order to have a better insight into the structure evolution of nanoparticle-stabilized double emulsions based on viscous polymer blends, a more detailed analysis of droplet dynamics (coalescence and breakup) under flow in the presence of nanoparticles is needed. Moreover, the role of structural characteristics (including diameter, shape, and aggregation) and surface nature of nanoparticles in controlling the behavior of double emulsions should be paid close attention since they are reported to have pronounced effects on the morphology of simple systems.[34,49–51] Systematic studies based on model emulsions filled with better particles (such as spherical particle[52,53]) rather than the complex particles used here would be more helpful.

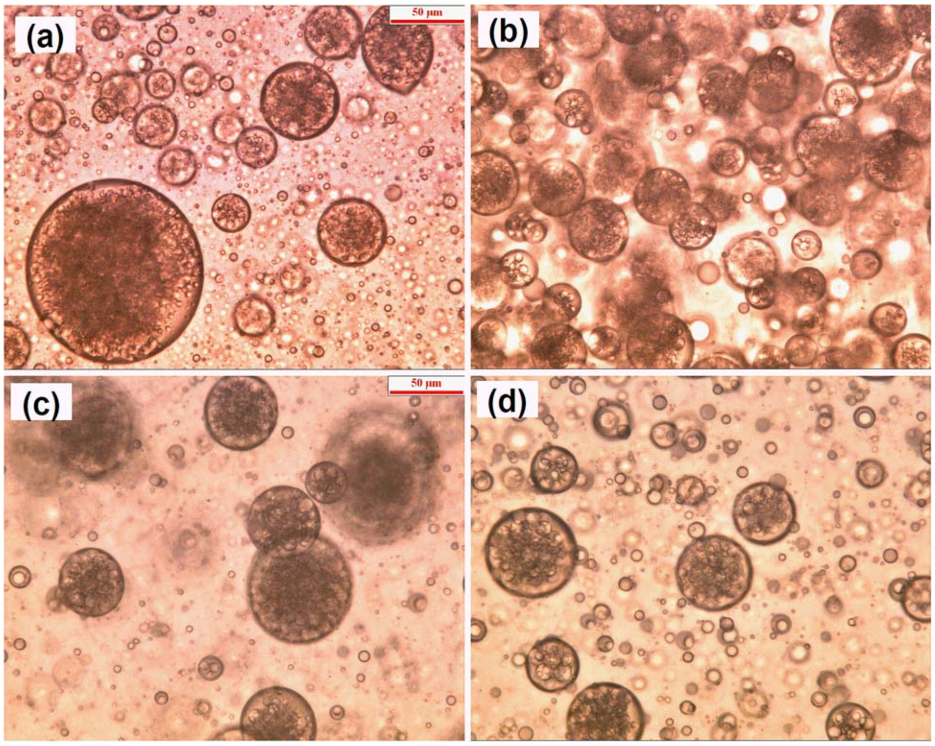

Figure 11. Morphologies of samples with different compositions: (a) B20–0.8 as prepared; (b) B20–0.8 after shearing at 0.5 s^{-1} for 8000 s; (c) B10–0.8 as prepared; (d) B10–0.8 after shearing at 0.5 s^{-1} for 8000 s.

The scale bars denote 50 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

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