

Coalescence Suppression in Flowing Polymer Blends Using Silica Rods with Different Surface Chemistries

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Abstract Silica rods with homogeneous (hydrophilic or hydrophobic) and amphiphilic surface properties were synthesized and their efficiencies in suppressing the flow-induced droplet coalescence of immiscible polyisobutylene (PIB)/polydimethylsiloxane (PDMS) blends were evaluated *via in situ* visualization technique. The flow-induced coalescence behavior of blends was found to strongly depend on the surface nature and concentration of silica rods added as well as the blend ratio. While a trace amount of rods promoted coalescence, all kinds of rods demonstrated a morphology refinement effect at high rod concentrations. Good compatibilization effects were obtained at high rod concentrations, especially for hydrophilic and amphiphilic rods. Based on confocal laser scanning microscopy results, these phenomena observed were interpreted reasonably in terms of the selective distribution and aggregation of silica rods, which were suggested to be decisive for the stabilization mechanism and efficiency of these rods.

Keywords Immiscible polymer blends; Flow; Morphology; Silica rods; Surface chemistry

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INTRODUCTION

Once being adsorbed at a liquid-liquid interface, micro or nanoscale solid particles are extremely difficult to detach^[1] and thus form a mechanically robust barrier preventing coalescence between adjacent droplets. Therefore, water/oil or oil/water emulsions stabilized with solid particles, also known as Pickering-Ramsden emulsions,^[2,3] can be created, which have tremendous applications in fields such as cosmetics, food, and pharmaceuticals.^[4] In fact, a similar idea is also prevalent in the polymer community. By using solid particles to manipulate the structure of immiscible polymer blends, novel functional materials with superior properties can be obtained.^[5–7] It has been found that the surface chemistry of particles, such as hydrophilicity or hydrophobicity, determines to a large extent whether particles locate in one particular phase or at the interface, which is essentially crucial for tailoring the stability and type of blends.^[8] For particles located preferentially inside the dispersed phase or the matrix phase, the increased viscosity of phase will also suppress the coalescence process by retarding the rupture and drainage of matrix film or by increasing the merging time of droplets.^[9,10]

Besides the surface chemistry, solid particles can also possess a variety of shapes (such as spherical, rod-like, ellipsoidal, disk-like, fractal, and so on) according to the material nature

and synthesis route. Nowadays, the role of particle wettability, particle size, and particle concentration during the structure formation of particle-laden blends has been studied in great detail by using near-spherical particles^[11,12] and fractal fumed particles^[11,12] in the last few decades. Meanwhile, blends stabilized with shape-anisotropic particles, such as carbon nanotubes,^[13] cellulose nanocrystals,^[14] calcium carbonate (CaCO₃) rods,^[15] ellipsoidal polystyrene (PS)^[16,17] and ferric oxide (Fe₂O₃) particles,^[16] have also been receiving increasing interest. Owing to the stronger attractive capillary interaction^[18] and ability to form percolation network^[14] or jam the interface, anisotropic particles offer greater potential in controlling the stability of blends than their counterparts.

On the other side, amphiphilic particles with chemical anisotropy, which are often referred to as “Janus” particles, combine the merits of both the amphiphilicity of molecular surfactants and the mechanical robustness of solid particles.^[19,20] In oil/water systems, the amphiphilic Janus particles are reported to possess considerably higher activity in reducing the interfacial tension than homogeneous nanoparticles of comparable size and chemical nature.^[21] Janus particles are expected to adsorb at the interface with their hydrophobic part inside the oil phase and hydrophilic part inside the water phase, which generates stronger attachment and superior stabilization ability.^[19,21] Additionally, Janus particles with asymmetric morphology such as rod-like, dumbbell-like, and discs have also been found to emulsify liquids efficiently and have a higher interfacial activity than homogeneous ones.^[22,23] In polymer blends, Janus particles can lead to optimized structures and improved mechanical properties due

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to their preferential distribution at the interface.^[24,25]

The morphological response of particle-laden blends subjected to flow can provide valuable information on microstructure during processing or application. There are some reports which concern the flow-induced droplet coalescence or breakup of blends stabilized by spherical or fumed silica particles.^[26–28] However, reports about the flow behavior of blends stabilized by rod-like particles with different surface chemistries are still scarce. Our previous studies^[17,29] showed that compared with PS microspheres, interfacially active PS ellipsoids not only promoted flow-induced droplet coalescence but also induced the formation of irregular droplets at lower loadings. In the case of amphiphilic silica rods,^[30] we found that the flow-induced morphology of blends at a high shear rate strongly depends on the rod concentration and blend ratio.

This study aims to compare the morphological stabilization effect of silica rods with homogenous or amphiphilic surface nature toward polymer blends in slow shear flow. First, three kinds of silica rods are prepared following a facile one-pot route.^[31,32] Then, different concentrations of silica rods are used to stabilize immiscible polyisobutylene (PIB)/polydimethylsiloxane (PDMS) 10/90 and 90/10 blends subjected to slow shear flow. Both PIB and PDMS are nearly Newtonian fluids with low viscosities at the experimental temperature (30 °C), which allows for a reasonable particle diffusion and droplet dynamics. Also, the fluidic nature of both components avoids the problem of thermal degradation which is frequently encountered in polymer melts during long-term shear experiments. The PIB/PDMS blend forms a typical droplet/matrix structure at a blend ratio of 10/90 or 90/10. Taking these advantages of this model blend, the flow-induced morphology of blends in the presence of silica rods are investigated by using *in situ* optical-shear microscopy and confocal laser scanning microscopy (CLSM) and discussed in terms of the preferential distribution and aggregation of silica rods.

EXPERIMENTAL

Preparation and Characterization of Silica Rods

Hydrophilic silica rods were synthesized using a simple one-pot method proposed by Kuijk *et al.* as follows.^[31] Firstly, 2.8 mL of deionized water, 1 mL of anhydrous ethanol, 1 mL of sodium citrate solution (180 mmol/L in water), and 2 mL of ammonia (28 wt%) were added into a solution of 10 g of polyvinylpyrrolidone (PVP) and 100 mL of *n*-pentanol. The mixture was stirred for 2 min before tetraethoxysilane (TEOS) was added and left to rest at room temperature for about 6 h. The solution was then centrifuged at 8000 r/min for 30 min and washed with the ethanol and water five times at 6000 r/min for 15 min. Hydrophobic silica rods were synthesized by simply modifying hydrophilic rods using dichlorodimethylsilane (DCDMS) at 130 °C for 1 h.

Amphiphilic silica rods with a similar length to that of homogeneous ones were synthesized according to the method proposed by He *et al.*,^[32] which is a derivative method of Kuijk *et al.*^[31] In this method, hexadecyltrimethoxysilane (HDTMOS) was introduced to grow the hydrophobic block after the hydrolytic condensation of TEOS and reacted for another 6 h.

The mixture was then centrifuged and washed as hydrophilic rods did.

The geometrical parameters of rods were examined by scanning electron microscopy (SEM, JEOLJSM-5900VL). The surface chemical properties of rods were detected using Fourier transform infrared spectroscopy (FTIR) in the transmittance mode on a Nicolet 6700 FTIR spectrometer. The spectra were collected in the 4000–650 cm^{−1} range at a resolution of 4 cm^{−1}.

Preparation of Blend Samples

Polyisobutylene (PIB, Daelin Industrial Co., Ltd., Korea) and polydimethylsiloxane (PDMS, Aldrich, America) were used for all experiments. The zero-shear viscosity of PIB and PDMS at 30 °C was 78 and 96 Pa·s, respectively. The PDMS had lower surface tension ($\gamma=19.2$ mN/m) but a slightly higher polarity ($\gamma_p=0.8$ mN/m) than PIB ($\gamma=32.1$ mN/m, $\gamma_p=0.4$ mN/m) at 25 °C.^[33,34] Silica rod-filled PIB/PDMS (10/90, W/W) blends were prepared in two steps. Firstly, silica rods were dried at 120 °C for at least 6 h to get rid of water and then added into PDMS in a small flask. Blending was conducted fiercely by hand with a spatula until no large aggregates were visible under the optical microscope. Then, PIB was added into the above mixture and stirred until a homogenous and white creamlike liquid was attained. After that, the mixture was vacuumed overnight at 40 °C to remove the entrapped air bubbles before shear experiments. 90/10 Blends were also prepared in a similar method. The silica rod concentration considered was 0.1 wt%, 0.2 wt%, 0.4 wt%, 0.8 wt%, 2.0 wt%, and 4.0 wt% based on the total weight of blends.

Morphological Characterization

Optical microscopy

Shear experiments were carried out at 30 °C in a Linkam CSS450 shearing hot stage (Linkam Scientific Instruments, UK) mounted on an Olympus microscope equipped with a long working distance objective (20×) and a Fixcelly CCD camera. The shear cell consisted of two parallel glass plates. The bottom plate was rotated at a controlled speed while the top one was fixed. The observation window on the top plate was 7.5 mm from the center. The gap between the two plates was fixed at 300 μ m in this study. Before each coalescence experiment, samples were preconditioned by shearing at $\dot{\gamma}=20$ s^{−1} for 300 s to eradicate the sample history. Subsequently, these well-dispersed samples were coalesced by stepping down the shear rate to a predefined value of $\dot{\gamma}=0.1$ s^{−1}, at which shear-induced coalescence was dominant. The strain units used in the experiments were 2000, corresponding to a shear time of 2.0×10^4 s, at which equilibrium blend morphologies were obtained. The droplet size was determined from optical micrographs using the free ImageTool software. Typically, 200 droplets were analyzed per sample. The volume-averaged radius (R_v) of droplets was calculated by

$$R_v = \frac{\sum_{n=1}^{\infty} n_i R_i^4}{\sum_{n=1}^{\infty} n_i R_i^3} \quad (1)$$

with R_i as the radius of each droplet and n_i as the number of droplets having radius R_i .

Confocal laser scanning microscopy

To probe the distribution of silica rods in the liquid blends, silica rods with a uniform fluorescence level were prepared. Firstly, a

certain amount of rods were added into 25 mL of deionized water, and then the mixture was sonicated for 1 min. As hydrophobic silica rods were difficult to disperse in water, 25 mL of the mixture of deionized water and ethanol was adopted instead of only deionized water. Subsequently, 5 mg of water-soluble Rhodamine B (Sigma-Aldrich) was added into the rod suspension obtained to stain rods for about 2 h under magnetic stirring.^[32] Afterward, stained rods were vacuum filtered and washed with deionized water for several times to remove extra dyes. PIB/PDMS blend samples with rods after the shearing experiment were transferred onto a glass slide by spatula and covered with coverslip carefully to avoid the artificial morphology and particle position changes. Fluorescence images were then taken by using a Leica TCS SP5II confocal laser scanning microscope (CLSM) with a 63× oil immersion objective under the excitation of 553 nm laser at room temperature.

RESULTS AND DISCUSSION

Properties of Silica Rods

Figs. 1(a)–1(c) show the SEM images of silica rods prepared and the corresponding dimensions of these rods are summarized in

Table 1. Hydrophilic and hydrophobic rods have similar shapes with a flat end and a rounded end. For amphiphilic rods, tadpole-like morphology is observed consisting of a solid and rigid hydrophilic head linking with a hollow hydrophobic tail.^[32] These rods have a length of ~2.0 μm and an aspect ratio of ~6. These silica rods are not visible in the optical images due to their small size. The surface nature of these rods is examined by FTIR (Fig. 1d). In Fig. 1(e), hydroxyl index (I_{OH} , 3450 cm⁻¹) and silanol index ($I_{\text{Si-OH}}$, 950 cm⁻¹) were calculated to quantitatively evaluate the concentration of hydrophilic groups, whereas that of the hydrophobic groups was determined by calculating the methyl index (I_{CH_3} , 2960 cm⁻¹) and the methylene index (I_{CH_2} , 2920 and 2854 cm⁻¹). The corresponding peak intensities were normalized according to the peak area at 800 cm⁻¹ which corresponds to the Si–O stretching vibrations. Fig. 1(d) shows that hydrophilic rods have a relatively high hydroxyl index and silanol index. However, no methylene (–CH₂–) or methyl (–CH₃) groups are found for hydrophilic rods, implying their inherent hydrophilicity. In contrast, hydrophobic and amphiphilic rods show two characteristic absorbance bands at 2960 and 2920 cm⁻¹ representing methyl and methylene groups, respectively. Fig. 1(e) shows that the hydrophobic rods possess

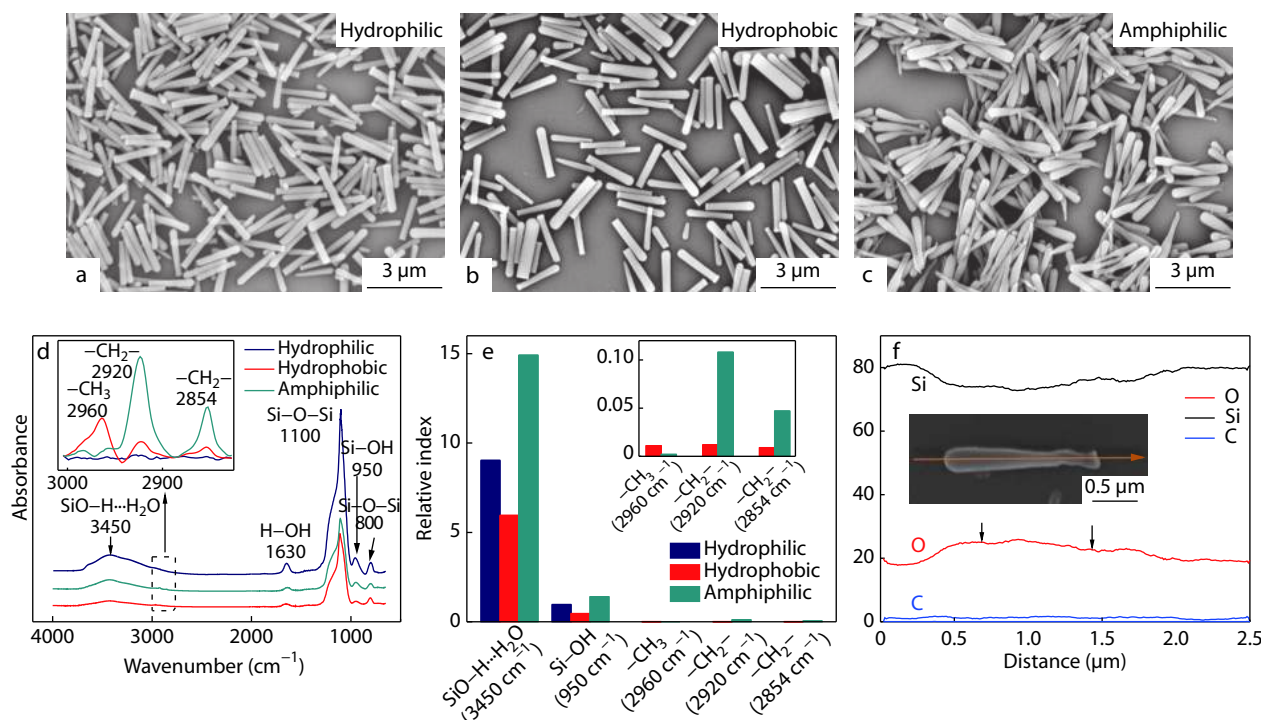


Fig. 1 SEM images of silica rods: (a) hydrophilic rods; (b) hydrophobic rods; (c) amphiphilic rods. Surface properties of rods: (d) unnormalized FTIR spectra; (e) relative index of different groups; (f) normalized element content profiles obtained by energy dispersive spectrometer (EDS) along the long axis of an amphiphilic rod.^[30]

Table 1 Dimensions of synthesized silica rods.

	l^a (μm)	d^a (μm)	l_1^b (μm)	l_2^b (μm)	d_1^c (μm)	d_2^c (μm)	l_1/l_2	AR ^d
Hydrophilic	1.9±0.1	0.3±0.1	—	—	—	—	—	6.3±1.4
Hydrophobic	2.0±0.2	0.3±0.1	—	—	—	—	—	6.5±1.3
Amphiphilic	2.0±0.2	—	0.9±0.1	1.1±0.1	0.3±0.01	0.2±0.04	0.8±0.1	6.0±1.0

^a l and d are the average length and diameter of silica rods, respectively; ^b l_1 and l_2 are the average lengths of the hydrophilic and hydrophobic blocks of amphiphilic rods, respectively; ^c d_1 and d_2 are the average diameters of the hydrophilic and hydrophobic blocks of amphiphilic silica rods, respectively; ^d Aspect ratio (AR) of amphiphilic rods was the ratio of its overall length l to diameter d_1 .

fewer silanol groups than hydrophilic rods, suggesting that the reaction of silanol groups with DCDMS led to only a moderate hydrophobicity for hydrophobic rods.

It is noticed that the amphiphilic rods display a much higher silanol index even than that of hydrophilic rods, which may be explained by the contribution from the internal and external surface of their hollow hydrophobic tails. However, this does not mean that these rods are more hydrophilic than hydrophilic rods. The introduction of long alkyl chains by hexadecyltrimethoxysilane should endow amphiphilic rods with hydrophobicity in the hydrophobic ends while keeping sufficient silanol groups untouched in the hydrophilic ends. Energy dispersive spectrometer analysis along the long axis of amphiphilic rods (Fig. 1f) reveals that the oxygen concentration on the rod surface varies from a higher level in the large hydrophilic head to a lower level in the small hydrophobic end, implying the hydrophilic head contains more oxygen-containing functional groups than the hydrophobic end. The surface tension of PIB, PDMS, hydrophilic and hydrophobic rods are listed in Table 2. Based on the FTIR, EDS and surface tension results, the hydrophilic rods should have a better affinity to the PDMS phase with a higher polarity while the hydrophobic rods modified with DCDMS prefer locating at the PIB/PDMS interface in consideration of surface tension.^[33,34]

Table 2 Surface tension of materials.

	γ (mN/m)	γ_d (mN/m)	γ_p (mN/m)
PIB	32.1	31.7	0.4
PDMS	19.2	18.4	0.8
Hydrophilic rods	80	29.4	50.6
Hydrophobic rods	32	30	2

γ_d and γ_p stand for the dispersive and the polar contributions to the surface tension, respectively.

For amphiphilic rods, they are expected to present a behavior between that of hydrophilic ones and hydrophobic ones.

Flow-induced Coalescence Behavior

Blends filled with hydrophilic rods

Figs. 2(a)–2(d) and 2(a')–2(d') compare the flow-induced morphology ($\dot{\gamma}=0.1\text{ s}^{-1}$, $2.0\times 10^4\text{ s}$) of PIB/PDMS blends with diverse ratios (10/90 and 90/10) in the presence of various amounts of hydrophilic silica rods. Corresponding volume average radius (R_v) and normalized volume average radius (R_v/R_{v0}) of droplets are summarized in Figs. 2(e) and 2(f). For all blends, a typical island-sea structure is formed, in which discrete spherical or ellipsoidal domains are dispersed in the matrix. Upon the addition of extremely low concentrations (e.g. $\phi_{\text{rod}}=0.1\text{ wt\%}$) of rods, the 10/90 blend (Fig. 2b) displays a notable increase in the phase size and a wide size distribution.

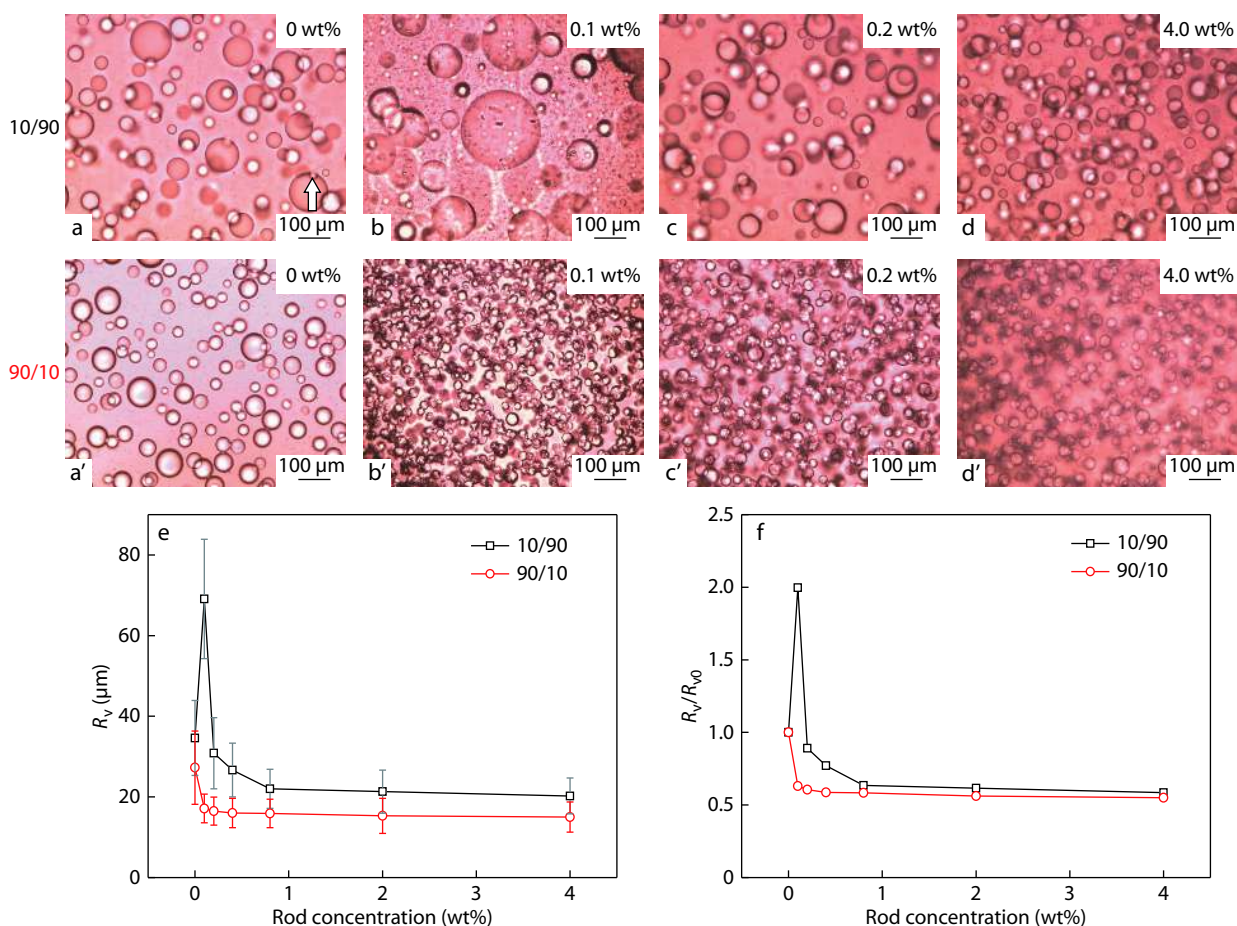


Fig. 2 Optical microscopy images of (a–d) 10/90 and (a'–d') 90/10 PIB/PDMS blends filled with different concentrations (0 wt%–4.0 wt%) of hydrophilic rods after shearing at $\dot{\gamma}=0.1\text{ s}^{-1}$ for $2.0\times 10^4\text{ s}$. The arrow in (a) shows the flow direction. (e) Volume-averaged radius (R_v) and (f) normalized R_v (R_v/R_{v0}) of droplets in PIB/PDMS blends as a function of hydrophilic rod concentration.

However, incorporating more rods leads to a continuous decline and homogenization in the droplet size, suggesting the compatibilization effect of hydrophilic rods toward the blends. A similar “promotion-to-suppression” phenomenon has been reported by Nagarkar *et al.*^[35] for poly(ethylene oxide) (PEO)/PIB blends stabilized with interfacially active spherical particles. For the 90/10 blends (Figs. 2b'–2d'), in contrast, the droplet size declines monotonously upon the addition of hydrophilic rods, and no promoted coalescence is found. The normalized R_v curves (Fig. 2f) suggest that hydrophilic rods have a slightly better compatibilization effect in the 90/10 blends than in the 10/90 blends. Upon the addition of 0.2 wt% hydrophilic rods, the droplet radius (R_v) of 90/10 blends declines by 40% from 27.5 μm for the neat blend to 16.5 μm for the rod-filled blend. In both cases, the R_v levels off at relatively low ϕ_{rod} , implying the limited compatibilization capability of hydrophilic rods. The critical ϕ_{rod} for R_v to level off is 0.8 wt% for the 10/90 blend while it decreases to 0.2 wt% in the 90/10 blend (Fig. 2e). Overall, hydrophilic rods have only a moderate compatibilization ability toward the PIB/PDMS blends.

Blends filled with hydrophobic rods

Compared with hydrophilic rods (Fig. 2), hydrophobic rods (Fig. 3) lead to a more profound “promotion-to-suppression” transition in the coalescence behavior for both the 10/90 and

90/10 blends. The rod concentration for the occurrence of promoted coalescence increases to 0.2 wt%–0.4 wt% (Fig. 3a). Moreover, unlike the case of hydrophilic rods, the promoted droplet coalescence by hydrophobic rods is very profound in the 90/10 blend rather than in the 10/90 blend. The R_v increases from 27.5 μm for the neat 90/10 blend to 66.0 μm for the filled one, resulting in an increase of 150% in the size. As the ϕ_{rod} further increases, however, the droplet size declines dramatically within the ϕ_{rod} range investigated (up to 4 wt%). Especially, hydrophobic rods result in a more noticeable droplet refinement in the 10/90 blend than in the 90/10 blend. Upon the addition of 4 wt% rods, the R_v decreases by 88% to 4.4 μm . In contrast, the decline amplitude of droplet size in the 90/10 blend is only 67%. Compared with hydrophilic rods (Fig. 2), hydrophobic ones demonstrate a much superior ability in refining the flow-induced morphology of PIB/PDMS blends at high ϕ_{rod} .

Besides the change in droplet size, hydrophobic rods also induce a notable change in the shape of droplets from spherical into irregular (Figs. 3c and 3c') at moderate ϕ_{rod} of 0.4 wt%–0.8 wt%. The presence of non-spherical droplets is usually resulting from “arrested coalescence” caused by particle jamming at the surface of adjacent coalescing droplets.^[36,37] Herein, the arrested coalescence occurs at a

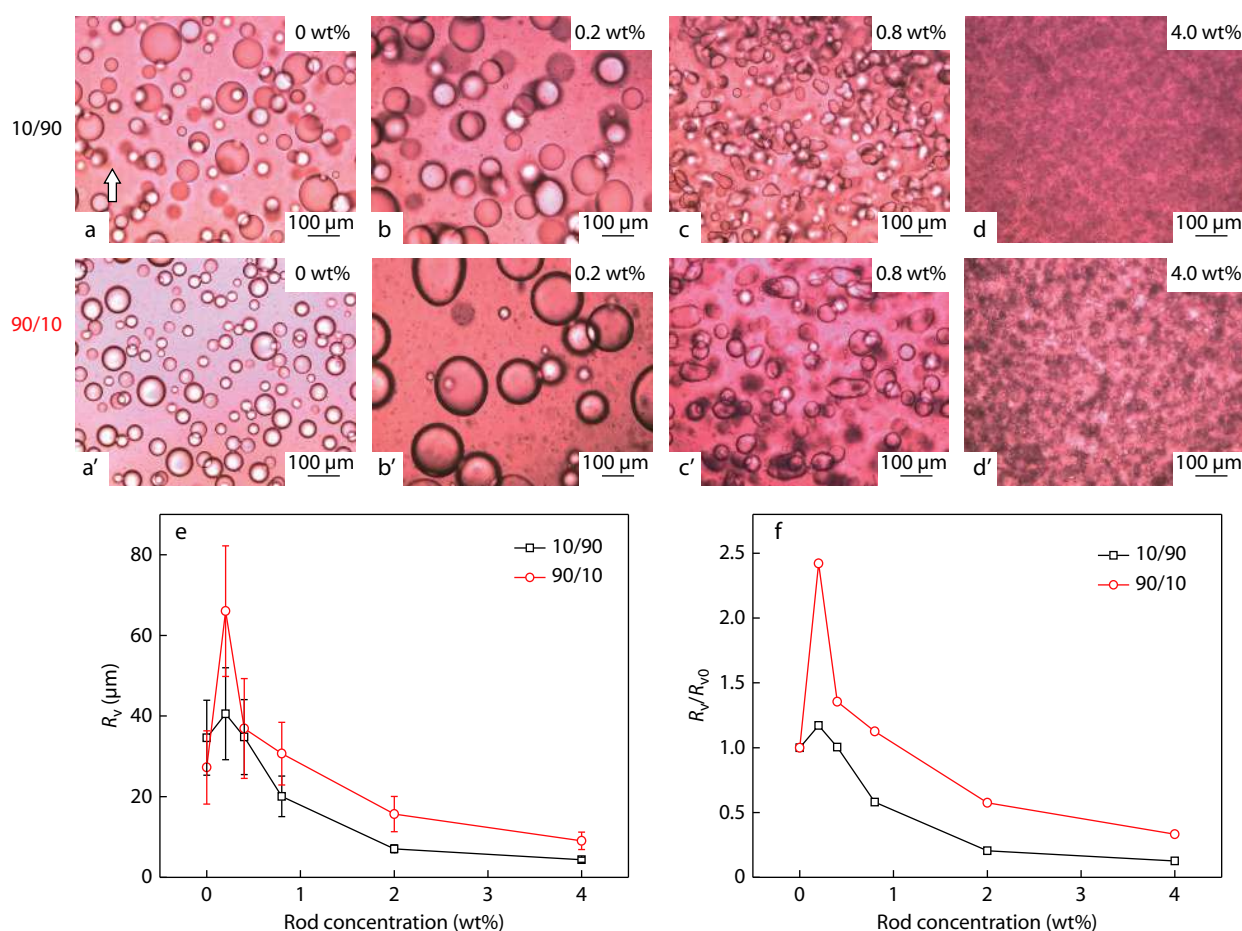


Fig. 3 Optical microscopy images of (a–d) 10/90 and (a'–d') 90/10 PIB/PDMS blends filled with different concentrations (0 wt%–4.0 wt%) of hydrophobic rods after shearing at $\dot{\gamma}=0.1 \text{ s}^{-1}$ for $2.0 \times 10^4 \text{ s}$. The arrow in (a) shows the flow direction. (e) Volume-averaged radius (R_v) and (f) normalized R_v (R_v/R_{v0}) of droplets in PIB/PDMS blends as a function of hydrophobic rod concentration.

rather low ϕ_{rod} of 0.4 wt% (not shown here), suggesting that a considerable amount of hydrophobic rods should locate at the interface between droplets and the matrix. Another interesting observation is that these anisotropic droplets formed *via* arrested coalescence, instead of aligning in the flow direction, align in the direction perpendicular to the flow direction, namely in the vorticity direction, in both blends (Fig. 3c and Figs. 3c'). A similar phenomenon has also been reported in our previous studies with PS ellipsoids and microspheres^[17,38,39] and interpreted by using the Jeffery orbits theory^[40] in the framework of fluid mechanics. It is suggested that only when oriented in the vorticity direction can these rigidized droplets rotate around their long axes under slow shear flow with a minimized energy dissipation. It should be noted that both the “arrested coalescence” and vorticity alignment behavior are hard to be discerned (Figs. 3d and 3d') at high ϕ_{rod} such as 4.0 wt%. It can be understood by the significant increase in the total surface area of dispersed droplets upon the addition of 4 wt% rods. Taking the 10/90 blend as an example, as the ϕ_{rod} increases from 0.8 wt% to 4.0 wt% (5 folds), the R_v decreases rapidly from 30.7 μm to 9.1 μm , implying a large increase of surface area by 11 folds. Therefore, the calculated ϕ_{rod} on the surface of droplets in the 10/90 blend with 4.0 wt% rods should be much lower than

that of the blend with 0.8 wt% rods and may be not high enough to induce interfacial jamming.

Blends filled with amphiphilic rods

Similar to the other two kinds of rods, amphiphilic rods also cause a “promotion-to-suppression” transition in the droplet size of flowing PIB/PDMS blends, regardless of the blend ratio. For both blend ratios, amphiphilic rods promote droplet coalescence at a low ϕ_{rod} of 0.2 wt% (Figs. 4b and 4b') while lead to a noticeable morphological refinement upon increasing the loading amounts (≥ 0.8 wt%) (Figs. 4c, 4d, 4c' and 4d'). However, several distinct features can be identified. The most notable one is that the amphiphilic rods display a similar compatibilization effect on both 10/90 and 90/10 blends at high ϕ_{rod} , namely a decline sensitivity of compatibilization efficiency on the blend ratio, which differs significantly from hydrophobic rods. This result also differs from our previous study^[30] carried out at a higher shear rate of 0.5 s^{-1} , in which the compatibilization effect of amphiphilic rods showed a stronger dependence on the blend ratio. This clearly indicates that the shear condition should also play a role in determining the compatibilization behavior of rods. The insensitivity of the stabilization efficiency of amphiphilic rods to the blend ratio should be the desired merit in practice. It is because that when these rods are used to compatibilize polymer blends, a strict

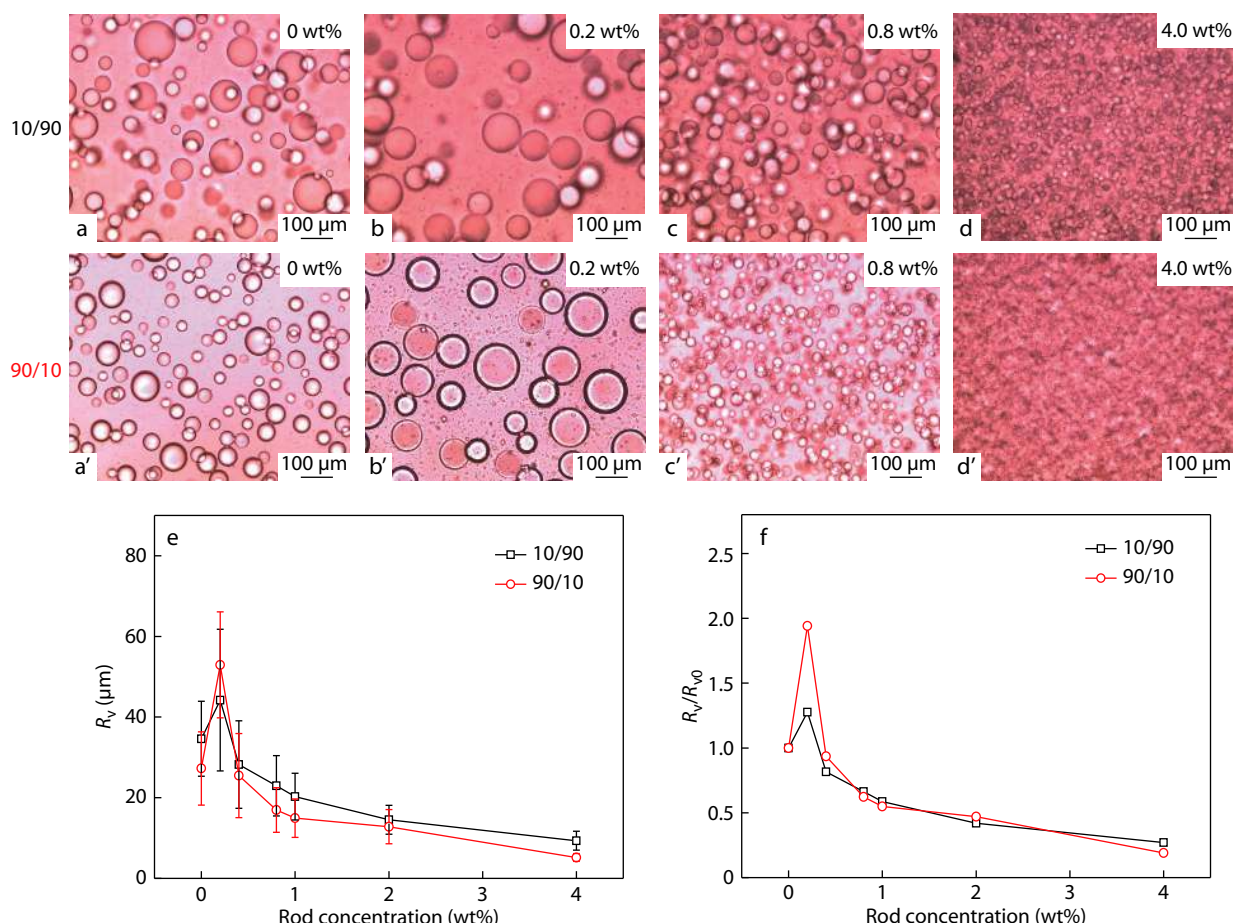


Fig. 4 Optical microscopy images of (a–d) 10/90 and (a'–d') 90/10 PIB/PDMS blends filled with different concentrations (0 wt%–4.0 wt%) of amphiphilic rods after shearing at $\dot{\gamma}=0.1 \text{ s}^{-1}$ for $2.0 \times 10^4 \text{ s}$. The arrow in (a) shows the flow direction. (e) Volume-averaged droplet radius (R_v) and (f) normalized R_v (R_v/R_{v0}) of blends as a function of amphiphilic rod concentration.

formulation is not required. Besides, neither irregular shape nor vorticity alignment of droplets is found in amphiphilic rod filled blends within the ϕ_{rod} range investigated (0 wt%–4 wt%), suggesting the absence of interfacial jamming at the droplet surface. Overall, the hydrophilic rods possess a compatibilization efficiency comparable to that of hydrophobic rods.

Possible Mechanisms for the Discrepancy in Stabilization Efficiency

The above morphology characterization results show that the flow-induced coalescence behavior of droplets strongly depends on the surface nature and concentration of silica rods as well as the blend ratio. Considering the importance of the location of silica rods on the blend morphology, fluorescence-labeled rods stained with trace Rhodamine B dye were prepared and their selective distributions in the blends were determined by using confocal laser scanning microscopy (CLSM). The fluorescence labeling is found not to alter the behavior of rods in these blends.^[30] Fig. 5 shows the CLSM images of sheared PIB/PDMS blends filled with 0.4 wt% stained rods which appear red under the fluorescence microscope.

It can be found that the distributions of these rods are not consistent with the prediction based on surface tension. In most cases, rods can hardly be found in the PDMS phase with a higher polarity but also a higher viscosity, regardless of whether the PDMS is a dispersed phase or a matrix phase. This implies that the viscosity of phases may play a role in determining the distribution of rods besides the thermodynamic parameter (surface energy), as found in previous studies.^[41–43] For hydrophilic rods, they mainly locate unevenly along the PIB/PDMS interface of 10/90 blends (Fig. 5a) in the form of large aggregates rather than reside in the more viscous PDMS matrix phase. This could be explained by the

strong trapping effect of the liquid-liquid interface toward rods during mixing,^[1] which decreases the total interfacial energy of whole systems. Interfacially located particles could promote coalescence by a “bridging-dewetting” mechanism (Fig. 6)^[44] or a “gluing-coalescence” mechanism.^[35] The former mechanism occurs when adjacent droplets are bridged by particles into proximity, thereby giving rise to droplet coalescence by dewetting the matrix film.^[44] The latter mechanism takes effect when two droplets are glued together by few interfacial particles, thereby facilitating the contact and merging of the uncovered surface area of two droplets.^[35] These mechanisms could explain the formation of large droplets upon the addition of 0.1 wt% hydrophilic rods as found in Figs. 2(b) and 2(b'). For the 10/90 blend with 0.4 wt% hydrophilic rods, such promoted coalescence behavior is hardly identified possibly due to the higher concentration of rods at the PIB/PDMS interface which prevents contact of the uncovered area between adjacent droplets. In the 90/10 blends, hydrophilic rods prefer to distribute in the PIB matrix phase with low viscosity in an aggregated form (Fig. 5a'). The poor dispersion of hydrophilic rods in the matrix phase is unfavorable for the effective stabilization of droplets *via* mechanisms such as the steric hindrance of interfacial particle layer^[1] or retarded rupture/drainage of matrix film.^[10] Therefore, hydrophilic rods only display a limited morphological refinement effect toward PIB/PDMS blends as revealed in Fig. 2, in which rod-induced rheological enhancement of blends may play a role in suppressing the droplet coalescence.^[8]

For hydrophobic rods, Figs. 5(b) and 5(b') reveals that as expected, they are mainly trapped at the PIB/PDMS interface regardless of the blend ratio. As a result, promoted coalescence is expected both in the 10/90 and 90/10 blends

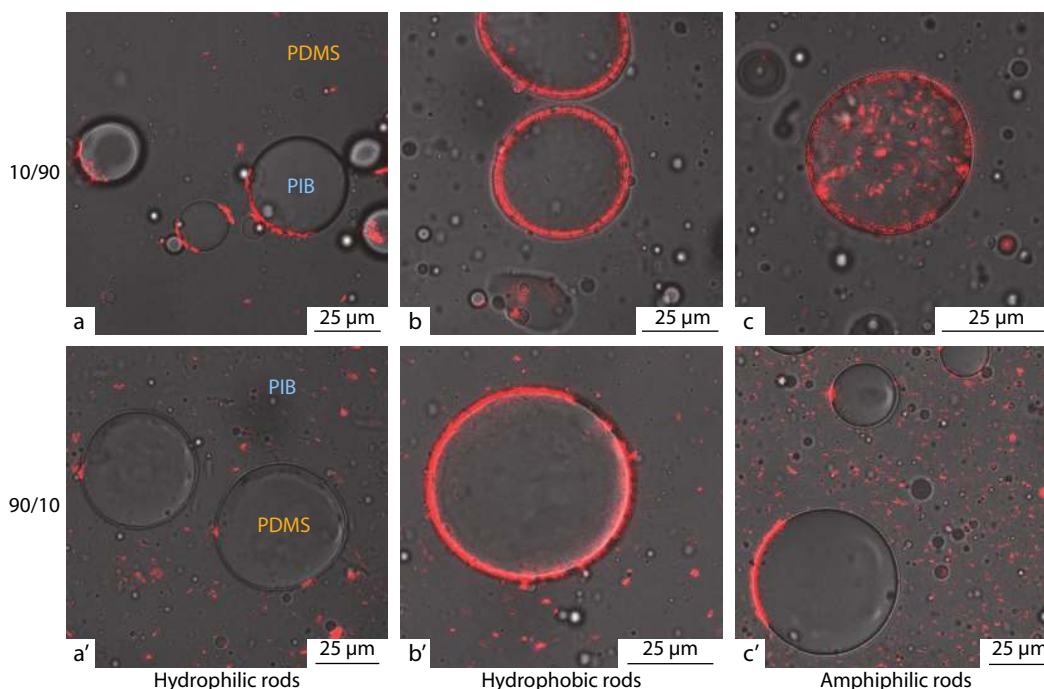


Fig. 5 Overlapped CLSM images of PIB/PDMS blends filled with 0.4 wt% rods obtained in the fluorescence and bright field mode: (a–c) 10/90 blends with hydrophilic, hydrophobic or amphiphilic rods stained with Rhodamine B (appear red); (a'–c') corresponding rod-filled 90/10 blends.

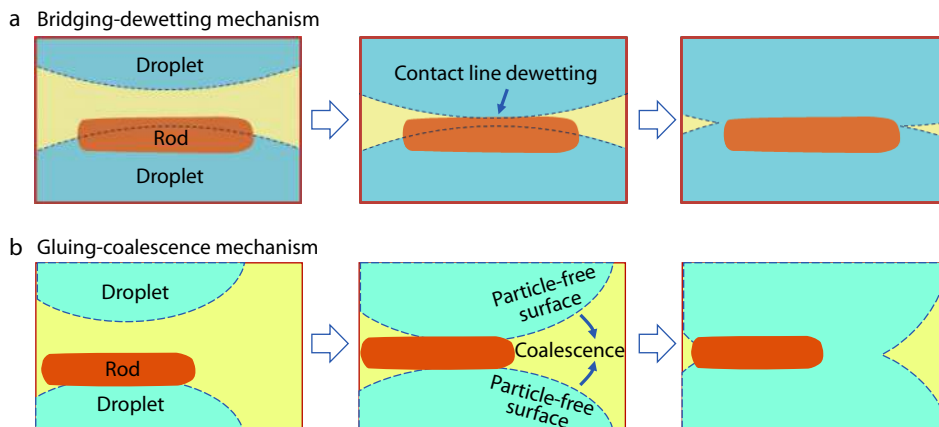


Fig. 6 Mechanisms of promoted coalescence in PIB/PDMS blends in the presence of silica rods in shear flow: (a) bridging-dewetting; (b) gluing-coalescence. The phase with a convex surface denotes the droplet phase.

(Figs. 3b and 3b') at very low ϕ_{rod} (0.1 wt%–0.2 wt%) via the “briding-dewetting” mechanism or “gluing-coalescence” mechanism. As the ϕ_{rod} further increases to 0.4 wt%–0.8 wt%, tightly packed rod layers form and fully cover the surface of droplets (Figs. 5b and 5b'), thereby effectively jamming the interface and leading to the formation of non-spherical droplets via arrested coalescence under flow (Figs. 3c and 3c'). These anisotropic particle-covered droplets formed resemble rigid particles suspended in a Newtonian fluid, adopting a vorticity alignment in slow shear flow (with a near-zero Reynolds number) to fulfill the requirement of the lowest energy dissipation.^[40] At higher ϕ_{rod} (>0.8 wt%), the high interfacial coverage can effectively suppress droplet coalescence and thus result in significantly refined morphology.

To further infer the packing behavior of hydrophobic rods (≥ 0.4 wt%) at the PIB/PDMS interface on the morphology of blends, a quantitative correlation between the droplet size and the rod concentration required is established. It is assumed that all hydrophobic rods are confined at the interface and form a monolayer coverage. For a droplet with a radius of R , the concentration ($\phi_{\text{rod,full}}$) required for rods to realize a full monolayer interfacial coverage with their length direction parallel to the interface can be calculated by

$$\phi_{\text{rod,full}} = \frac{m_{\text{rod}}}{m_{\text{drop}} \times \phi_{\text{drop}}} = \frac{\frac{4\pi R^2}{ld} \times \pi \left(\frac{d}{2}\right)^2 l \rho_{\text{rod}}}{\frac{4}{3}\pi R^3 \rho_{\text{drop}} \times \phi_{\text{drop}}} \quad (2)$$

where m_{rod} is the mass of rods on a droplet, m_{drop} is the mass of a droplet, ϕ_{drop} is the blend ratio (equals 0.1 here), l and d are the length and diameter of rods, ρ_{rod} and ρ_{drop} are the density of silica rods (2.2 g/cm³) and droplets (0.90–0.96 g/cm³), respectively. From Eq. (2), the theoretical droplet size versus ϕ_{rod} curve at $\phi_{\text{rod}} \geq 0.4$ wt% can be calculated and shown in Fig. 7. The experimental curve of the hydrophobic rod-filled PIB/PDMS (10/90) blend coincides satisfactorily with the predicted R_v - ϕ_{rod} curve, suggesting that hydrophobic rods should mainly form a thin monolayer at the liquid-liquid interface in this blend. However, the experimental curve of the hydrophobic rod-filled PIB/PDMS (90/10) blend is above the predicted R_v - ϕ_{rod} curve, suggesting that some rods do not locate at the interface and the assumption of a fully interfacial rod monolayer may become

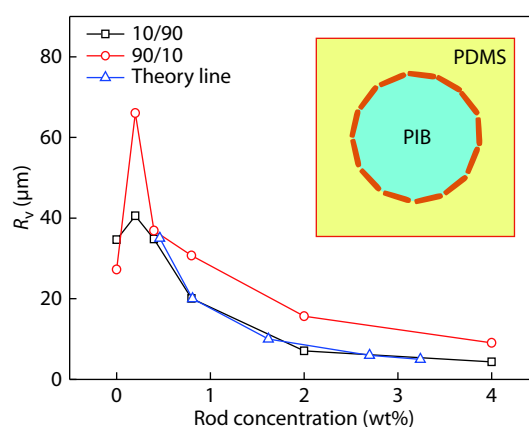


Fig. 7 Comparison of experimental and theoretical droplet size (R_v) versus rod concentration (ϕ_{rod}) in hydrophobic rod filled PIB/PDMS blends. As the theoretical lines of 10/90 and 90/10 blends almost overlap, only one theory line is shown in this figure.

invalid. This corresponds well with the fact that the interfacial layer in the 90/10 blend is somewhat thicker than that in the 10/90 blend and some hydrophobic rods can also be found sporadically within the PIB matrix (Fig. 5b'). The latter fact also embodies the preferential affinity of these interfacially located hydrophobic rods toward the PIB matrix phase in the 90/10 blend. Therefore, hydrophobic rods demonstrate a lower coalescence suppression efficiency than in the 10/90 blend. It should be noted that the arrangement of particles at the liquid-liquid interface has a great influence on the structure of blends. Other techniques such as scattering may provide more valuable information about the details of particle orientation at the interface.^[45]

For amphiphilic rods, Fig. 5(c) shows that they mainly disperse uniformly within the PIB droplets in the 10/90 blend although some of them also present at the liquid-liquid interface. It has been suggested that the transfer dynamics of particles at the blend interface have a strong dependence on particle shape and slim particles have faster dynamics than those of fat ones.^[46] Here, the sharp hydrophobic tails of amphiphilic rods may facilitate these rods passing across the PIB/PDMS interface, thus leading to the preferential enrich-

ing of amphiphilic rods in the PIB droplets with a lower viscosity.^[41] Similar to hydrophobic rods, few amphiphilic rods located at the interface promote droplet coalescence at low ϕ_{rod} (Fig. 4b) and the underlying reason can also be understood by using a similar fashion. At higher ϕ_{rod} (≥ 0.8 wt%–1.0 wt%), the amphiphilic rods will cover more interface area and form steric hindrance against coalescence. Also, those amphiphilic rods resided in the droplets tend to get networking,^[17] giving rise to enhanced viscoelasticity which is capable of retarding coalescence. Both effects will contribute to the suppression of droplet coalescence. However, a full interfacial coverage could not be achieved as no arrested coalescence is found in this blend. In the 90/10 blend, amphiphilic rods distribute mainly within the matrix (PIB) phase (Fig. 5c') while some of them also present at the liquid-liquid interface. Therefore, promoted flow-induced droplet coarsening is also expected at low rod loadings (Fig. 4b). At high rod concentrations, benefiting from the preferential distribution of amphiphilic rods, the viscoelasticity of the PIB matrix phase is expected to be improved and therefore prohibit the flow-induced coalescence of droplets by retarding the film rupture/drainage process of the matrix phase.^[8] As a result, the droplet size declines with increasing ϕ_{rod} . Therefore, amphiphilic rods exhibit good compatibilization efficiency both in 10/90 and 90/10 blends, leading to a low sensitivity on the blend ratio. It should be noted that due to the low viscosity of PIB/PDMS blends, reliable rheological experiments cannot be carried out in the present study to illustrate the effect of rod-induced blend morphology and therefore would be the emphasis of our future work.

CONCLUSIONS

The selective location and aggregation of silica rods in flowing PIB/PDMS blends depended largely on their surface nature and were critically essential to their compatibilization efficiencies toward the blends. It was found that the tendency of rods to distribute at phase with a lower viscosity may interfere with the presence of a liquid-liquid interface. The trapping of a trace amount (0.1 wt%–0.2 wt%) of rods at the liquid-liquid interface was prone to induce catastrophic droplet coalescence. For hydrophilic rods, their severe aggregation at high concentrations resulted in only a limited compatibilization effect. In contrast, both the hydrophobic and amphiphilic rods exhibited satisfied refinement effects at high rod concentrations, which may lead to better mechanical properties of blends. Hydrophobic rods might form an interfacial hindrance layer at the liquid-liquid interface, and their capacity in suppressing droplet coalescence depended largely on the blend ratio. Interfacial jamming of hydrophobic rods caused the arrested coalescence at moderate rod concentrations (0.4 wt%–0.8 wt%) and led to the formation of vorticity-aligned droplets under slow flow. For amphiphilic rods, their good dispersion and networking within the dispersed phase or matrix phase resulted in a high stabilization efficiency which was insensitive to the blend ratio. Therefore, strict formulations are not required when amphiphilic rods are employed as compatibilizers. It is believed that the findings reported here should provide some new insight into the rational design of new efficient particle compatibilizers for polymer blends.

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