Morphology Mapping of Nanoparticle-Filled Immiscible Polymer Blends in Flow: The Existence of a Critical Ratio between Nanoparticle Concentration and Droplet Concentration

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Supporting Information

ABSTRACT: The delicate flow-induced morphology of immiscible polypropylene/polystyrene blends in the presence of silica nanoparticles (NPs) is investigated in a multiparameter space. The morphology map constructed based on in situ morphology observation reveals that a critical ratio of NP concentration to droplet concentration, which strongly depends on the NP surface chemistries and the ratio of the NP concentration to the droplet concentration, exists. Below or above the critical ratio, the NPs display diverse effects on the morphology (promote or suppress droplet coalescence). These results can be interpreted by the competition between the bridging mechanism (acceleratory effect) and the enhanced viscoelasticity (inhibitory effect) exerted by the NPs.

INTRODUCTION

Inorganic nanoparticles (NPs) have been purposefully used as modifiers to improve the mechanical, barrier, and thermal properties of immiscible polymer blends because it is low-cost in industrial application.1−3 The properties of filled blends depend largely on the final morphology generated during the structure evolution, such as the coalescence and breakup behavior of droplets, experienced during melt processing.4−9 Most of available researches focus on the final morphology and properties of ternary immiscible blends,10−26 but it is still arguable how NPs affect the dynamics of morphology evolution during flow (processing).27−32

In ternary particle/liquid/liquid mixtures, such as Pickering emulsions,10−12 bijels,13−15 and “dry liquids”,16,17 the morphology evolution is found to mainly depend on the surface chemistries of particles, the wettability of particles and components, the loadings of particles, and the blend ratio. For example, Velankar et al.18−21 in detail investigated how these factors simultaneously affect the morphology of ternary mixtures. Specifically, in interfacially active particle-filled polyethylene oxide (PEO)/polyisobutylene (PIB) blends with a droplet/matrix morphology, the size of the dispersed phase can be increased and reduced at low (~0.1 vol %) and high (~1 vol %) volume fractions of particles through promoting the flow-induced coalescence and completely covering the interface, respectively; however, when particles are preferentially wetted by the continuous phase, the morphology consists of clusters of particle-bridged drops.20 When particles are almost completely wetted by one of the polymer phases, increasing the wetting fluid loading induces a morphological transition from a pendular network to compact capillary aggregates network, with an intermediate funicular state.21 Moreover, a composition-morphology map is constructed in PIB/PEO/particle blends, which reveals that particles affect the morphology greatly when the dispersed phase (PEO) is prefered by the particles.23

However, until now, there is yet no scientific consensus on how NPs affect the morphology evolution of blends in flow, and increasing research is dedicating to gain more insights into the morphology and properties of NP-filled blends. For instance, in the polypropylene (PP)/polystyrene (PS) 70/30 blend,33 the morphology is significantly refined both by 3 wt % hydrophobic silica located at the interface because of the inhibited coalescence of the PS dispersed phase and by 3 wt %...
RESULTS AND DISCUSSION

Distribution of NPs in Blends. The distribution of A200 and R974 silica NPs in filled PP/PS blends is characterized by transmission electron microscopy (TEM), respectively. Figure 1a,c reveals that most of A200 NPs disperse exclusively in the PS phase and a small portion of them locate at the interface of PS and PP (as shown by red arrows). Diversely, although lots of R974 NPs locate within the PS phase, they are closer to the interface between PP and PS (Figure 1b,d). This agrees well with the distribution of NPs in blends predicted by the wetting parameter ($\omega_{12}$). The $\omega_{12}$ is defined as $\omega_{12} = (\gamma_{Si,o} - \gamma_{Si,n})/\gamma_{12}$ (where $\gamma_{Si,o}$ is the interfacial tension between the silica NP and the polymer i and $\gamma_{12}$ is the interfacial tension between the two polymers). When $\omega_{12} > 1$ ($\omega_{12} < -1$), silica NPs are present only in polymer 1 (polymer 2). For $-1 < \omega_{12} < 1$, the NPs should be located at the interface between the two polymers. Then, $\omega_{12} = 4.93$ and 2.19 for A200- and R974-filled PP/PS blends, respectively, where the details of this calculation are given in our previous papers.36,37 This indicates that A200 NPs mainly disperse in PS phase while R974 NPs also locate in PS phase but are closer to the interface, which agrees the TEM results.

Morphology of NP-Filled Blends. First, the initial morphology of all as-prepared PS/PP blends is investigated, as shown in Figures S1−4 (see in the Supporting Information). For all as-prepared PS-minor blends, a typical droplet/matrix structure is found. However, the near-spherical PS droplets get refined with increasing NP concentration, regardless of the hydrophilic (A200) or hydrophobic (R974) nature of NPs (Figures S1 and 2). For all as-prepared PP-minor blends, the morphology becomes coarsened with increasing concentration of hydrophilic (A200) NPs (Figure S3) while it becomes refined with increasing the concentrations of hydrophobic (R974) NPs (Figure S4). Moreover, the rheological properties for all as-prepared PP/PS blends are shown in Figures S5 and S6. The storage moduli and complex viscosities for all samples are shown to increase with the NP concentration, especially when the NP concentration exceeds 3 wt %. In addition, for a given NP concentration, viscoelasticity of hydrophilic NP-filled blends is much higher than that of hydrophobic filled ones.

Figure 1. TEM images showing the location of 1 wt % A200 (a) and R974 (b) NPs in PS-minor (PS20) blends and 1 wt % A200 (c) and R974 (d) NPs in PP-minor (PP20) blends. The scale bars in images a–d denote 100 nm, 0.2 μm, 0.5 μm, and 0.5 μm, respectively.
Different from the peculiar morphology evolution in PS-minor blend, ellipsoidal, and fibrillar PP droplets always form in PP-minor blends upon introducing A200 NPs (Figure S8). Increasing ϕ_{PP} will increase the number of fibrillar droplets while increasing ϕ_{R974} will make most of PP droplets fibrillar and larger (Figure S8c,d,g,h,k,l). Dense fibrillar PP droplets with a radial size of 10–15 μm and length beyond 250 μm are observed in the PP10-AS blend (Figure S8h) and with radial size up to 60 μm appear in the PP20-AS blend (Figure S8i).

For hydrophobic NP (R974)-filled PS minor blends, the morphology also strongly depends on the relative content of R974 NPs (ϕ_{R974}) and PS dispersed phase (ϕ_{PS}). As the ϕ_{R974} and ϕ_{PS} vary, either refined or coarsened PS droplets are observed, as shown in Figure 3 (PS-minor blends filled with more different concentrations are shown in the Figure S9). For example, for R974-filled PS systems, with increasing ϕ_{R974}, the PS droplets first get coarsened and then refined (Figure 3a–d), demonstrating a critical ϕ_{R974} of about 1.5 wt % (Figure S9a–f). As the ϕ_{PS} increases to 10% (Figure 3e–h) and 20% (Figure 3i–l), the critical ϕ_{R974} increases to 3 wt % (Figure S9g–l) and 6 wt % (Figure S9m–r), respectively. Differently, in R974-filled PP-minor blends, PP droplets are refined remarkably at ϕ_{R974} = 1 wt % (reducedt to 25, 32, and 56% of their initial droplet size, as shown in Figures S10 and S11) and then are refined with further increasing ϕ_{R974} (Figures S10 and S11). Therefore, 1 wt % R974 NPs can be defined as critical ϕ_{R974} which is similar to the critical micelle concentration of copolymer in compatibilized blends.38

State Map and Mechanism. On the basis of the above results, the morphology evolution of NP-filled PP/PS blends is diagrammed in Figure 4 in a multiple parameter space consisting of the blend ratio (ϕ_{PS}), NP loading and surface nature (ϕ_{A200} or ϕ_{R974}). Obviously, for A200-filled PS minor blends, the role of NPs on the phase structure at low ϕ_{PS} and ϕ_{A200} is opposite to the case with high ϕ_{PS} and ϕ_{A200}, suggesting the existence of a critical ratio of NP to droplet concentration (red dash line in Figure 4a). On this critical line, the critical ratio (ϕ_{A200}/ϕ_{PS}) of ϕ_{A200} to ϕ_{PS} equals ~0.2. Below this line (namely, ϕ_{A200}/ϕ_{PS} < ~0.2), A200 NPs coarsen droplets and above this line A200 NPs refine droplets. As shown in Figure 4b, a similar critical rule can also be found when adding R974 NPs into PS-minor blends. However, the critical ratio (ϕ_{R974}/ϕ_{PS}) increases to ~0.3, below which coarsened PS droplets are present while above which the morphology becomes refined.

The delicate effect of NPs on the ϕ_{NP}/ϕ_{drop} ratio is believed to be closely related to the changes in the interfacial and viscoelastic properties of blends induced by the distribution of NPs. The TEM images in Figure 1 reveal that most of A200 NPs disperse exclusively in the PS phase and a small portion of them locate at the interface of PS and PP. Diversely, although lots of R974 NPs locate within the PS phase, they are closer to the interface between PP and PS. As most of NPs selectively disperse in the PS phase, the viscoelasticity of corresponding PS/A200 and PS/R974 composites is enhanced accordingly with increasing ϕ_{NP} (ϕ_{A200} or ϕ_{R974}) as shown in Figure 5, especially for PS/A200 composites at low frequencies. For PS-minor blends, A200 NPs locate mainly within the PS droplets, as shown in the TEM image in Figure 1a. When ϕ_{A200}/ϕ_{PS} is below the critical value (<~0.2), only a small portion of A200 NPs locate at the interface of PS droplets and PP matrix, which cannot fully cover the surface of PS droplets (as shown by red arrows in Figure 1a). Therefore, when two filled PS droplets

Figure 2. Optical micrographs of hydrophilic silica NP (A200)-filled PP/PS blends with PP as a matrix: (a–d) PP/PS 95/5 (PSS) blends, (e–h) PP/PS 90/10 (PS10) blends, and (i–l) PP/PS 80/20 (PS20) blends unfilled and filled with different concentrations (1, 3, and 5 wt %) of A200 (A1, A3, and A5) NPs after shearing at 0.1 s⁻¹ and 200 °C for 7000 s, respectively. The scale bar denotes 50 μm. The red arrow represents the direction of shear flow.

Figure 3. Optical micrographs of hydrophobic silica NP (R974) filled PP/PS blends with PP as a matrix: (a–d) PP/PS 95/5 (PSS) blends, (e–h) PP/PS 90/10 (PS10) blends and (i–l) PP/PS 80/20 (PS20) blends unfilled and filled with different concentrations (1, 3 and 5 wt %) of R974 (R1, R3 and R5) NPs after shearing at 0.1 s⁻¹ and 200 °C for 7000 s, respectively. The scale bar denotes 50 μm. The red arrow represents the direction of shear flow.
collide during shearing, A200 NPs on the surface of one PS droplet may stick onto the uncovered surface of the other PS droplet (Figure 6a,b) and tend to make droplets coalesce. However, the interface relaxation of these coalescing droplets is significantly suppressed due to the enhanced viscoelasticity of filled PS droplets (Figure 5a,b). As a result, large irregular PS droplets which cannot relax into ellipsoidal or spherical droplets are formed. A similar phenomenon was also found in
the PA6/PS (20/80) blend with A200 NPs selectively filling in PA6 phases. The critical value \( \phi_{\text{PA6/PS}} \) of 0.2), A200 NPs tend to form aggregates and networks within PS droplets which greatly enhance the viscoelasticity of droplets (Figure 5a,b), leading to much longer coalescence time.39 Besides, more A200 NPs will locate at the surface of PS droplets. Both will make droplets more rigid and prevent the effective coalescence upon collision (Figure 6c). As a result, significantly refined morphology is observed in blends with high \( \phi_{\text{A200}} \) (Figure 2c,d,g,h).

Differently, in R974-filled PS-minor blends, R974 NPs locate within PS droplets but are more close to the blend interface (Figure 1b). Below the critical value \( \phi_{\text{R974/PS}} \) (0.3), the NPs on the partially covered PS droplets enable the "bridging-dewetting mechanism" to work. As shown in Figure 7, when one PS droplet is in close proximity to another droplet, surface is not protected by NPs, and in slow flow, the edge of the bridged layer ruptures, allowing coalescence to proceed (Figure 7b). Then, bridged and coarsened PS droplets form. A similar phenomenon was found in ternary PEO/PIB/silica systems because of the preferential wetting of silica particles by the PIB matrix, and in PDMS/PIB 90/10 blends with A200 NPs selectively filling in the PDMS matrix.

In R974-filled PP-minor blends, R974 NPs locate within the PS matrix and form a layer at the blend interface (Figure 1d). As shown in Figure 4b, the PP droplets are gradually refined with increasing \( \phi_{\text{R974}} \) regardless of the \( \phi_{\text{PP}} \) (Figure S10). The refined PP droplet size can be ascribed to the prevented coalescence of PP droplets by the formation of R974 NP layer in PS matrix close to the interface of blends (Figures 1d and 7e,f).33 With further increasing \( \phi_{\text{R974}} \), the PP droplet size changes little.

Overall, in PS-minor blends, if most of A200 NPs disperse exclusively in PS droplets and a small portion of them locate at the interface between PS droplet and PP matrix (Figure 1a), the PS droplets become coarsened below the critical \( \phi_{\text{A200/PS}} \) (0.2) and the coalescence of droplets is suppressed above the critical value. If lots of R974 NPs locate within PS droplets and are close to the interface between PS droplet and PP matrix (Figure 1b), the coalescence of PS droplets is promoted below the critical \( \phi_{\text{R974/PS}} \) (0.3) and suppressed above the critical value. Here, below the critical \( \phi_{\text{PP}} \), the coarsened morphology agrees well with the reports that if the particles are located on the interface but wetting the droplet polymer, bridges can also form but not so stable that coalescence may happen. In PP-minor blends, if most of A200 NPs disperse exclusively in PS matrix and a small portion of them locate at the interface between PP droplet and PS matrix (Figure 1c), the formation of fibrillar PP droplets is promoted. If lots of R974 NPs locate within the PS matrix and are close to the interface between PP droplet and PS matrix (Figure 1d), fibrillar PP droplets are refined. Here, the morphology of R974-filled PP minor blends agrees well with the reports that if the particles are located on the interface and wetting the continuous polymer, particles can stabilize the droplets and even act as bridge to form stable droplet clusters. However, the morphology of A200-filled PP minor blends differs. Most A200 NPs distributed in matrix and a small portion of A200 NPs located at the interface lead to the destabilization of the droplets under flow.
CONCLUSIONS

In summary, the morphology evolution in silica NP-filled PP/PS blends under slow flow strongly depends on the surface chemistry and loading of NPs (φ_{NP}) and weight fraction of droplets (φ_{dop}). When NPs tend to locate in droplets, or are close to the interface and in droplets, the morphology evolution of filled blends exhibits a critical rule related to φ_{NP}/φ_{dop}. Below the critical φ_{NP}/φ_{dop}, NP-induced bridging and droplet coalescence is dominated, resulting in coarsened and irregular droplets. However, beyond the critical φ_{NP}/φ_{dop}, the droplet coalescence can be suppressed because of enhanced viscoelasticity, and droplets are refined effectively. This critical φ_{NP}/φ_{dop} is found to change with the surface chemistry and distribution of NPs, and is ∼0.2 for hydrophilic NPs and ∼0.3 for hydrophobic NPs. Such a critical rule is not found when NPs disperse in the matrix or are close to the interface and in the matrix. Fibrillar droplets are formed when hydrophilic NPs located in the matrix and refined droplets are formed when hydrophobic NPs dispersed interfacially.

EXPERIMENTAL SECTION

Materials. PP (T30S) was provided by Lanzhou Petrochemical Co. Ltd., and had a melt flow index (MFI) of 2.6 g/10 min (190 °C, 2.16 kg) and density of 0.91 g/cm³. PS (GP5250) was supplied by Taihua Plastic (Ningbo) Co., Ltd. and had a MFI of 7.0 g/10 min (200 °C, 5 kg) and density of 1.05 g/cm³. Fumed hydrophilic silica (Aerosil A200) and hydrophobic silica (Aerosil R974) were supplied by Degussa Corp. Both types of silica NPs (SiO₂) had an average primary diameter of 12 nm, and the specific surface area of 200 ± 25 and 170 ± 20 m²/g, respectively. Anti-oxidant 1010 (pentaerythritol tetракис-[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], purity > 95.0%) provided by Wuhan Petrochemical Company, China, was used to prevent the degradation of PP during blending and experiments. Prior to melt blending, the pellets of components were dried in vacuum at 70 °C for 24 h.

Sample Preparation. All samples were blended with using an internal mixer (XSS-300, Kechuang, China). The mixing chamber was filled with 42 cm³ of materials. The screw speed was 50 rpm. For all blends, three components, hydrophilic/hydrophobic silica, PS, and PP, with 0.1% anti-oxidant 1010, were loaded to the mixing chamber simultaneously and compounded at 200 °C for 10 min (after blending for 10 min, the torque was stable for all samples). Various loadings (0–5 wt %) of hydrophilic (A200, Degussa) and hydrophobic (R974, Degussa) fumed silica NPs (φ_{A200} or φ_{R974}) are incorporated in PP/PS blends with different blend ratios (5–20 wt % of PP or PS droplets, φ_{PP} or φ_{PS}). Here, NP-filled PP/PS blends are designated as DC-NL blends for brevity, where D denotes the dispersed phase, C represents the concentration of the dispersed phase, N delegates the types of silica NPs, and L stands for the loading of silica NPs in the blend. Taking PPS-A1 and PPS-R1 blends for example, it signifies the PP/PS 5/95 blend filled with 1 wt % A200 and R974 NPs, respectively. The mixed blends were then compression-molded in vacuum at 200 °C for 5 min into disk-like samples with a diameter of 25 mm and a thickness of 1.5 mm. In addition, the PS/SiO₂ composites were prepared to investigate the changes of viscoelasticity induced by the selective distribution of silica NPs with different surface chemistries. All samples were kept in vacuum at 70 °C for characteristics.

Transmission Electron Microscopy. A field-emission TEM (Tecnai G2 F20) equipment was utilized to verify the location of A200 and R974 NPs in filled blends. Cross sections of pressed blends were obtained by slicing the sample into thin films of about 80–100 nm thicknesses via a Leica EMUC6/FC6 microtome and then were stained by OsO₄ vapor for 8 h. The dispersion of NPs was then observed by using TEM at an acceleration voltage of 200 kV.

Rheology Measurements. Rheological properties of the components and blends were measured using a strain-controlled rheometer (ARES, TA instruments, USA) with a parallel plate geometry of 25 mm in diameter. Linear viscoelastic measurements of the composites were conducted at 200 °C under nitrogen atmosphere to prevent thermo-oxidative degradation. The shear strain amplitude is 2%, which was found to be within the linear viscoelastic regime, and the range of the frequency is from 100 to 0.02 rad/s.

Morphology Observation. The morphological evolution of PP/PS/SiO₂ blends in shear flow was visualized in a counter-rotating shear cell (CSS450, Linkam Scientific Instruments Ltd., UK) consisting of two quartz parallel disks, which was mounted on an optical microscope (Olympus BX51, Japan). The sample was loaded into the shearing stage, and then the temperature was elevated to 200 °C at a rate of 30 °C/min. The real-time observation of morphological evolution during shear flow was carried out at a gap width of 100 μm. Before each test, the gap width was referenced by focusing two lines on the two plates and ensured the deviation within ±5 μm. First, before the observation, the sample was shearing at 20 s⁻¹ for 300 s to avoid the flow history effect produced by sample loading. Then, flow-induced droplet coalescence behavior in the presence of NPs was investigated at a low shear rate of 0.1 s⁻¹ for 7000 s (At 0.1 s⁻¹ and 200 °C, the viscosity of PP and PS is 5600 and 5100 Pa·s, respectively). After this period of shearing, the morphology for all samples is stable over time. The morphological evolutions of blends during shear were recorded every 10 s with a Linksys32 DV image acquisition system and were analyzed using a home-developed digital image analysis software package. It is noted that the optical micrographs of the flow-induced morphology shown in the paper were taken after the flow momentarily stopped. The number averaged diameter (Dₙ) was calculated according to

\[ Dₙ = \frac{\sum D_i}{N} \]

where N is the number of droplets and Dᵢ is the droplet diameter. Approximately 300 droplets were measured for each blend.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02072.

Initial morphology of hydrophilic silica nanoparticle (A200) filled PP/PS blends with PP as a matrix; initial morphology of hydrophobic silica nanoparticle (R974) filled PP/PS blends with PP as a matrix; initial morphology of hydrophilic silica nanoparticle (A200) filled PP/PS blends with PS as a matrix; initial morphology of hydrophobic silica nanoparticle (R974)
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The authors declare no competing financial interest.

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