Reactive Nanoparticles Compatibilized Immiscible Polymer Blends: Synthesis of Reactive SiO₂ with Long Poly(methyl methacrylate) Chains and the in Situ Formation of Janus SiO₂ Nanoparticles Anchored Exclusively at the Interface

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ABSTRACT: The exclusive location of compatibilizers at the interface of immiscible binary polymer blends to bridge the neighboring phases is the most important issue for fabricating desirable materials with synergistic properties. However, the positional stability of the compatibilizers at the interface remains a challenge in both scientific and technical points of view due to the intrinsic flexibility of compatibilizer molecules against aggressive processing conditions. Herein, taking the typical immiscible poly vinylidene fluoride (PVDF)/polylactic acid (PLLA) blend as an example, we demonstrate a novel approach, termed as the interfacial nanoparticle compatibilization (IPC) mechanism, to overcome the challenges by packing nanoparticles thermodynamically at the interface through melt reactive blending. Specifically, we have first synthesized nanosilica with both reactive epoxide groups and long poly(methyl methacrylate) (PMMA) tails, called reactive PMMA-graft-SiO₂ (Epoxy-MSiO₂), and then incorporated the Epoxy-MSiO₂ into the PVDF/PLLA (50/50, w/w) blends by melt blending. PLLA was in situ grafted onto SiO₂ by the reaction of the carboxylic acid groups with epoxide groups on the surface of SiO₂. Therefore, the reacted SiO₂ particles were exclusively located at the interface by the formation of the Janus-faced silica hybrid nanoparticles (JSNp) with pregrafted PMMA tails entangled with PVDF molecular chains in the PVDF phase and the in situ grafted PLLA chains embedded in the PLLA phase. Such JSNp with a distinct hemisphere, functioning as compatibilizer, can not only suppress coalescence of PVDF domains by its steric repulsion but also enhance interfacial adhesion via the selective interactions with the corresponding miscible phase. The interfacial location of JSNp is very stable even under the severe shear field and annealing in the melt. This IPC mechanism paves a new possibility to use the various types of nanoparticles as both effective compatibilizers and functional fillers for immiscible polymer blends.

KEYWORDS: reactive blending, Janus SiO₂ particles, interfacial nanoparticle compatibilization, in situ reaction, immiscible polymer blends

1. INTRODUCTION

Polymer blending provides a practical and efficient strategy to fabricate desirable materials with synergistic properties which cannot be obtained by homopolymers. Nevertheless, most of the polymer pairs are thermodynamically immiscible due to the intrinsic low mixing entropy, leading to the morphology coarsening and finally the deterioration of mechanical performances by the inherent propensity. Thus, the compatibility of polymer components becomes a key issue to manipulate both the micromorphology and physical properties of blends, which relies largely on the interface between phases.

One of the classic approaches to strengthen the interface is the incorporation of a specific surface-active copolymer called the “compatibilizer.” Such copolymers, either premade or in situ formed during blending, will prefer to span the interface: they could take on the role as macromolecular surfactants to reduce interfacial tensions, suppress particle coalescence, enhance interfacial adhesion, and eventually achieve a finer phase morphology. Extensive research in past decades has confirmed that the copolymer formed in situ by reactive blending can facilitate a much better phase dispersion and thus render higher compatibilizing efficiency than the premade one.
instance, Inoue and co-workers successfully improved compatibility of the polyamide 6 (PA 6)/polyethylene (PE) blend with maleic anhydride grafted PE (PE-MAH) by reactive blending and suggested that the in situ formed copolymers exhibited a much better emulsifying efficiency. 19 Macosko and co-workers 20 indicated that an ethylene-glycidyl methacrylate-methyl acrylate terpolymer (PEGMA) was the highly efficient emulsifying agent for the polylactide (PLA)/polypropylene (PP) blend through coupling to the end group of PLA during the mixing process. However, the actual reactive compatibilizing process is confronted with crucial challenges. Due to the inherent flexibility of copolymers, such compatibilizers would be “pulled-out” or “pulled-in” readily from the interface under aggressive flow conditions to form micelles. 21-24 The inevitable migration of the in situ formed copolymer reduces the compatibilizing efficiency. 25-27 It is indeed still urgent and challenging to pursue new types of compatibilizers and to increase the interfacial-localization stability of emulsifier between polymers.

On the other hand, inorganic nanofillers, concurrently, are gaining attention to improve the interfacial miscibility of particular blends. 28-30 Owing to their high specific area and fine scale, nanofillers such as graphene oxide (GO), 31,32 clay, 33-35 carbon black (CB), 36 carbon nanotubes (CNTs), 37-39 nanosilica, 40-46 and fullerene 47 exhibit great potential to accommodate at the polymer-polymer interface with appropriate wetting parameters. 48 In addition, such interfacial nanofillers show a better seclusion capacity and stability than copolymer species even against intense shear field because of their inherent rigidity. 40-43,51,52 Improvement of compatibility depends mainly on the shape, size, and surface modification of nanofillers or the external processing field. Trifkovic et al. 48 previously determined the compatibilizing effect of nanoclays in polyethylene (PE)/poly(ethylene oxide) (PEO) blends. The nanoclay platelets preferentially jammed the interface by thermodynamic force and supplied complete inhibition of phase coarsening with only 1 wt % loadings. Recently, Schmalz and co-workers 58,59 used “patchy” CTNs as efficient emulsifier for poly styrene (PS)/poly(methyl methacrylate) (PMMA) blends. A significant decrease of PMMA-domain size was achieved with increasing patchy CTNs content, which was attributed to the selective swelling of CNTs toward the respective phase at the PMMA-PS interface. Recently, Cassagnau and co-workers 60,61 systematically investigated the influence of nanofiller shapes on the phase structures of polymer blends. On the basis of the rheological behaviors, they pointed out that the surface functionality of nanoparticles takes a critical role on morphological refinement in polymer blends. However, the potential feasibility of nanoparticles compatibilizing remains largely explored. One major reason is the deficiency on the thermal dynamic compatibilization. The location of nanoparticles at the interface is mostly kinetically controlled. Besides, since the main effect of nanoparticles is to prevent coalescence of polymer domains, rather than enhancing interfacial adhesion by molecular entanglements, it is challenging to compatibilize blends sufficiently at the molecular level without sacrificing mechanical properties. Moreover, this strategy seems laborious and system specific, making it relatively too expensive to be scaled up.

We considered that interfacial nanoparticle compatibilization (IPC) should be feasible to compatibilize immiscible polymer blends once the surface of the nanoparticles can entangle with binary components separately. The thermodynamic compatibilization by the nanoparticles not only improves the interfacial adhesion but also enhances the interfacial stability against the mechanical shear and the thermal annealing due to the rigid nanoparticle core. A new type reactive-hybrid nanoparticle compatibilizer with both long molecular tails and reactive groups is then conceived. The pregrafted long molecular tails and the in situ grafted polymer chains shall adjust their configuration by interacting selectively with the miscible components of a blend, and the nanoparticles with Janus-corona selectively located at the interface were in situ formed. Thus, a remarkably enhanced interfacial adhesion could be achieved.

In this work, we have first synthesized reactive nanosilica (Epoxy-MSiO2) with both reactive epoxy groups and PMMA chains via the “attaching onto” approach. The reactive nanosilica is then incorporated into well-characterized immiscible polyvinylidene fluoride (PVDF)/polyactic acid (PLLA) blends 8,14,15 through melt blending. The compatibilization effects of the Epoxy-MSiO2 are carefully characterized. It is found that the in situ formation of interfacial Janus-shell during blending could promote a stronger interaction between the PMMA (PLLA) hemisphere and its corresponding PVDF (PLLA) phase via molecular entanglements. Meanwhile, such nanoparticles exhibit an ordered arrangement at the PVDF/PLLA interface. We consider that the IPC mechanism might be of importance in emulsifying polymer alloys and could even achieve more advanced nanocomposites for industrial purposes.

2. EXPERIMENTAL SECTION

2.1. Materials. Methyl methacrylate (MMA, Shanghai Sinopharm Co., China, polymer grade) was washed with 5 wt % NaOH solution to remove moisture and then distilled with CaH2 under reduced pressure. 4,4'-Azobis (4-cyanovaleric acid) (ACVA, Acros Co., Belgium, analytical pure) was recrystallized from methanol before use. Tetrahydrofuran (THF, Shanghai Lingfeng Co., China, analytical pure) was refluxed over sodium/benzophenone complex and then distilled under high vacuum. Nanosilica with mean size of 20 nm/110 nm (Carbot bluestar Co., China) was dried in vacuum at 200 °C before use. All other reagents were purchased from Aldrich and used as received. All reactions were carried out under nitrogen condition unless otherwise stated. The PVDF (Mw = 1.05 × 105 g/mol, Mw/Mn = 2.0) and PLLA (Mw = 8.93 × 105 g/mol, Mw/Mn = 1.77) were used which were purchased from Kureha and Nature Works, respectively.

2.2. Synthesis of Reactive Nanoparticles. 2.2.1. General Procedure for Telomerization for Carboxyl Ended Poly(methyl methacrylate) (PMMA-COOH). PMMA-COOH was synthesized according to our previous work. 8 In a typical reaction, MMA (20 g, 0.2 mol), ACVA (0.56 g, 0.002 mol), Thio (Thioglycolic acid, 0.41 g, 0.0045 mol), and THF (100 mL) were added into a flask. The mixture was stirred at 60 °C for 4 h. The solution was then dissolved in acetone, precipitated into excess petroleum ether and distilled water, filtered and dried in vacuum to afford 11.2 g (yield: 55%) of white powder. GPC: Mn = 4600 g/mol, Mw/Mn = 2.4. 1H NMR (500 MHz, CDCl3): δ = 3.58 (s, 3H, −OCH3), 3.32−3.25 (t, 2H, −CH2S), 2.03−1.81 (m, 2H, −CH2), 1.2−1.83 (t, 3H, −CH3); FTIR (KBr): 3438 cm−1, 2995 cm−1, 1746 cm−1, 1470nm cm−1, 1443 cm−1, 1395 cm−1, 1260 cm−1, 1230 cm−1, 1185 cm−1, 1145 cm−1, 755 cm−1.

2.2.2. General Procedure for Exterior Functionalization of SiO2 with Epoxy Groups (Epoxy-SiO2). Epoxy-SiO2 was prepared similar to the method demonstrated in ref 56. SiO2 (6 g) was first dissolved into 250 mL of toluene, and the mixture was ultrasonicated for 15 min. 3-Glycidoxypropyl trimethoxysilane (GPTS, 3.5 g) was then added dropwise to the suspension. The reaction mixture was transferred into a flask and refluxed at 110 °C for 10 h under nitrogen. The resulting material was centrifuged and washed thoroughly with toluene or ethanol to remove the unreacted GPTS. The washing procedure was repeated three times, respectively, and Epoxy-SiO2 was dried under vacuum at 65 °C for 25 h.

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14359
2.2.3. General Procedure for Grafting PMMA-COOH Chains onto the Exterior Surface of E-SiO2 by “Grafting onto” Method (Epoxy-MSiO2). Epoxy-MSiO2 was synthesized by grafting PMMA-COOH onto Epoxy-SiO2 through ring-opening reaction in the presence of alkali catalyst. A typical procedure is as follows: Epoxy-SiO2 (2 g) was first dissolved into 80 mL of xylene and ultrasonicated for 5 min. Then, the solution containing PMMA-COOH ($M_\text{n} = 4600$ g/mol, 1 g, 0.25 mmol), $N,N'$-dimethylamylamine (amine, 0.0061 g, 0.045 mmol), and an extra 20 mL of xylene was added dropwise into the suspension, and the mixture was transferred into a flask and refluxed at 140 °C for 25 h. The resultant suspension was centrifuged and washed extensively with ultrasonication in toluene, THF, and acetone, respectively. Finally, the product was dried in vacuum at 65 °C for 24 h to afford 2.3 g (yield: 76%) of white powder.

2.2.4. General Procedure for Grafting PLLA Chains onto the Exterior Surface of Epoxy-SiO2 by “Grafting onto” Method (PMMA-random-PLLA)-g-SiO2, LM-SiO2). The LM-SiO2 was synthesized by the ring-opening reaction of carbonyl-terminated PLLA with the epoxy groups of Epoxy-SiO2. In a typical procedure, Epoxy-SiO2 (5 g) and PLLA (45 g) were premixed and added into the batch mixer (Haake Polylab QC) with a rotation speed of 50 rpm at 190 °C. The resultant sample was dissolved into chloroform and centrifuged. This procedure was repeated at least three times to completely remove the unreacted PLLA chains. The resulting LM-MSiO2 was dried under vacuum at 65 °C for 25 h.

2.3. Incorporation of Nanoparticles into PVDF/PLLA (50/50, w/w) Blends. The PVDF/PLLA (50/50, w/w) blends with various contents of SiO2, Epoxy-SiO2, or Epoxy-MSiO2 were fabricated by melt blending directly in a Haake Polylab QC mixer at 190 °C. These blends were prepared by mixing under the screw speed of 50 rpm for 10 min. The resulted blends were then compression molded at 200 °C under 10 MPa pressure for 6 min and quenched into liquid nitrogen. The obtained sheets with a thickness of 0.5 mm were applied directly in the MPa pressure for 6 min and quenched into liquid nitrogen. The resulted blends were then compression molded at 200 °C under 10 MPa pressure for 6 min and quenched into liquid nitrogen. The number-average diameter of PVDF domains ($d_n$) was calculated according to the following eq 2:

$$d_n = \frac{\sum N_i d_i}{\sum N_i}$$

where $N_i$ was the number and $d_i$ was the diameter of PVDF domain with $i \geq 300$.

Transmission electron microscopy (TEM, Hitachi HT-7700) was carried out to observe the distribution of nanoparticles in PVDF/PLLA blends at an accelerating voltage of 100 kV. The specimen was first ultramicrotomed to a section with the thickness of 80 nm and then stained with ruthenium tetroxide (RuO4) for 4 h at room temperature. Thus, the PVDF domains could be selectively stained and turned gray in TEM observations.

Dynamic mechanical analysis (DMA) was carried out using DMA Q-800 (TA Instrument) under nitrogen atmosphere. The specimens were then tested with a heating rate of 10 °C/min from −50 to 180 °C with the amplitude of 4 μm and the frequency of 5 Hz.

3. RESULTS

3.1. Preparation and Characterization of Epoxy-MSiO2

3.1.1. Synthesis of Epoxy-MSiO2: Functionalization of SiO2. As illustrated in Scheme 1, the reactive SiO2 with long PMMA chains (Epoxy-MSiO2) was synthesized by sequential immobilization of reactive epoxy groups and PMMA chains onto the exterior surface of SiO2 using silane coupling agent and PMMA-COOH, respectively. Such Epoxy-MSiO2 could take on the role of compatibilizer in immiscible polymer blends by reactive melt blending. The SiO2 particles with an average diameter of 16 nm were used as model nanoparticles. First, the pristine SiO2 was ginned and tableted with KBr, and then, such KBr plates were scanned from 4000 to 400 cm$^{-1}$ at a resolution of 2 cm$^{-1}$ with a minimum of 64 scans.

1H Nuclear magnetic resonance (1H NMR) and 29Si NMR measurements were performed on a Bruker Avance 500 spectrometer with CDCl3 as solvent. The operating frequency was 500 MHz.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Kratos Axis Ultra instrument with monochromatic Al Kα X-ray source. Wide scan was investigated in the range of 1300−0 eV, and the narrow scans were measured for the O 1s, C 1s, and Si 2p regions. The thermogravimetric analysis (TGA) was carried out on a TGA-Q500 (TA Instrument) in nitrogen atmosphere at a heating rate of 10 °C/min from 30 to 650 °C. The graft density of Epoxy-MSiO2 ($\sigma_{\text{Epoxy-MSiO2}}$) was calculated by the following equation:

$$\sigma_{\text{Epoxy-MSiO2}} = \frac{(1 - f_{\text{SiO}}) N_{\text{MSiO2}} d}{6f_{\text{MSiO2}} M_n}$$

where $f_{\text{SiO}}$ was the weight fraction of SiO2 in Epoxy-SiO2/Epoxy-MSiO2 determined by TGA measurement; $N_A$ was the Avogadro’s number; $\rho_{\text{SiO2}}$ was the density of SiO2; $d$ was the average diameter of SiO2; $M_n$ was the overall number-average molecular weight of polymer chains.

Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was performed to observe the morphologies of PVDF/PLLA blends at an accelerating voltage of 5.0 kV. The specimens were fractured by immersing in liquid nitrogen for 5 min and then spur-coated with gold. Besides, the number-average diameter of PVDF domains ($d_n$) was calculated according to the following eq 2:

$$d_n = \frac{\sum N_i d_i}{\sum N_i}$$

Here, $N_i$ was the number and $d_i$ was the diameter of PVDF domain with $i \geq 300$.

Transmission electron microscopy (TEM, Hitachi HT-7700) was carried out to observe the distribution of nanoparticles in PVDF/PLLA blends at an accelerating voltage of 100 kV. The specimen was first ultramicrotomed to a section with the thickness of 80 nm and then stained with ruthenium tetroxide (RuO4) for 4 h at room temperature. Thus, the PVDF domains could be selectively stained and turned gray in TEM observations.

Dynamic mechanical analysis (DMA) was carried out using DMA Q-800 (TA Instrument) under nitrogen atmosphere. The specimens were then tested with a heating rate of 10 °C/min from −50 to 180 °C with the amplitude of 4 μm and the frequency of 5 Hz.
Epoxy-MSiO2. Long PMMA chains were rooted readily on the adding a small amount of PMMA-COOH (step III) to synthesize pristine SiO2 (sample I), Epoxy-SiO2 (sample II), and Epoxy-MSiO2 (sample III), functionalized with epoxide groups by chemical modification using 3-glycidoxy-propyltrimethoxysilane (GPTS) to yield reactive SiO2 (Epoxy-SiO2) (step I). At the same time, PMMA-COOH with finely tuned molecular weight was synthesized by telomerization of MMA using ACVA as initiator and Thio as chain transfer agent (Scheme S-1, Table S-1, and Figures S-1 to S-3) (step II). Epoxy-SiO2 was then modified by adding a small amount of PMMA-COOH (step III) to synthesize Epoxy-MSiO2. Long PMMA chains were rooted readily on the surface of SiO2 with a covalent bond, which was attributed to the efficient nucleophilic cycloaddition reaction between epoxide groups of Epoxy-SiO2 and carboxyl groups of PMMA-COOH in the presence of alkali catalyst (N,N'-dimethyl laurylamine). Larger hybrid nanoparticles could be achieved through the same synthetic routes, using a pristine SiO2 with the diameter of 110 nm. Detailed information on the products was listed in Table 1. It should be noted that all reactions above were conducted under extremely mild conditions (moisture and atmosphere pressure), making it a reproducible preparation of hybrid nanoparticles for industrial production.

### 3.1.2. Characterization of Epoxy-MSiO2

Figure 1a shows the FTIR spectra of pristine SiO2, Epoxy-SiO2, and Epoxy-MSiO2. The intense bands at 3000 cm⁻¹ attributed to the stretching vibration of –CH from GPTS. This implied the occurrence of reaction between silica hydroxyl of pristine SiO2 and methoxyl of GPTS. Subsequently, a new peak at 1730 cm⁻¹ derived from carbonyl groups of PMMA segments appeared in Epoxy-MSiO2 (sample III). Since the unreacted PMMA-COOH was removed by extensive washing with organic solvents, the spectrum of Epoxy-MSiO2 indicated that the long PMMA chains were successfully grafted onto the exterior of Epoxy-SiO2 via the ring-opening reaction (step III). However, the intensity of the epoxide characteristic peak is too low to be observed before and after modification of SiO2. ¹H NMR (Figure 1b) demonstrated the appearance of epoxide (2.96 ppm, 2.89 ppm) and methoxyl (3.63 ppm) groups for Epoxy-MSiO2, providing the direct evidence of the reactive epoxide groups after the grafting reaction.

Figure 2 showed the XPS spectrum of pristine SiO2 and modified SiO2 nanoparticles. The major peak of all samples with the binding energy (BE) of 532.6 eV corresponded to O 1s element signal while the minor bands of 155.1 and 103.9 eV corresponded to Si 2s and Si 2p signals, respectively, which could be attributed to the existence of SiO2 core. As demonstrated in Figure 2a,b, the intensity of O 1s, Si 2s, and Si 2p was significantly reduced with the functionalization. Besides, a new peak at the BE of 285.3 eV assigned to C element signal was observed for both Epoxy-SiO2 and Epoxy-MSiO2 samples. The C 1s peak of Epoxy-MSiO2 turned much stronger than that of Epoxy-SiO2 (details

### Table 1: Molecular Parameter of PMMA-COOH and the Hybrid Nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g/mol)</th>
<th>$P$</th>
<th>$d$ (nm)</th>
<th>$T_g$ (°C)</th>
<th>$f_{SiO2}$ (%)</th>
<th>$\sigma_{SiO2}$ (nm⁻²)</th>
<th>$T_f$ (°C)</th>
<th>O 1s (atomic %)</th>
<th>Si 2p (atomic %)</th>
<th>C 1s (atomic %)</th>
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<tbody>
<tr>
<td>PMMA-COOH</td>
<td>4600</td>
<td>2.4</td>
<td>398.8</td>
<td>91.5</td>
<td></td>
<td></td>
<td></td>
<td>72.9</td>
<td>22.3</td>
<td>4.8</td>
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<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>68.0</td>
<td>19.3</td>
<td>12.7</td>
</tr>
<tr>
<td>Epoxy-SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>59.1</td>
<td>13.8</td>
<td>27.1</td>
</tr>
<tr>
<td>Epoxy-MSiO₂</td>
<td>4600</td>
<td>2.4</td>
<td>183.3 ± 0.5</td>
<td>1080</td>
<td>95.2</td>
<td>0.27</td>
<td>139.9</td>
<td>91.5</td>
<td>72.9</td>
<td>22.3</td>
</tr>
<tr>
<td>LSiO₂</td>
<td>110 ± 6</td>
<td>99.1</td>
<td>402.7</td>
<td>3.1</td>
<td>138.9</td>
<td>46.7</td>
<td>16.3</td>
<td>37.0</td>
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<tr>
<td>LEpoxy-SiO₂</td>
<td>115 ± 35</td>
<td>91.4</td>
<td>428.8</td>
<td>9.7</td>
<td>59.7</td>
<td>24.0</td>
<td>16.3</td>
<td>37.0</td>
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<tr>
<td>LEpoxy-MSiO₂</td>
<td>120 ± 37</td>
<td>63.0</td>
<td>403.7</td>
<td>3.1</td>
<td>138.9</td>
<td>46.7</td>
<td>16.3</td>
<td>37.0</td>
<td></td>
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</table>

* Determined by GPC plots using THF as eluent and linear PS as calibration at 35 °C ($M_n$: number-averaged molecular weight of PMMA chains; $P$: polydispersity ($M_w/M_n$) of PMMA chains). **Measured from TEM images ($d$: number-averaged diameter of nanoparticles). *Measured from the TGA curves of purified specimen ($T_g$: the TGA temperature with maximum loss rate; $f_{SiO2}$: inorganic content; $f_{org}$: organic content). ±Calculated by eq 1 on the basis of TGA data ($\sigma_{Epoxy-SiO2}$: graft density of PMMA chains). *Determined from DSC results ($T_g$: glass transition temperature of PMMA chains). ±Calculated from XPS spectrum. LSiO₂, LEpoxy-SiO₂, and LEpoxy-MSiO₂ referred to the nanoparticles with larger size ($d_{SiO2}$ = 110 nm).
shown in Tables 1 and S-2), suggesting that the PMMA-chain corona around SiO$_2$ was thick enough to shield most signals of SiO$_2$ core from XPS instrument. On the other hand, the O 1s signal of Epoxy-MSiO$_2$ had a decreased BE, as compared with SiO$_2$ and Epoxy-SiO$_2$ (Figure 2c). This indicated that the electron cloud density was changed due to the grafting reaction of PMMA long chains. To further identify the molecular structure in the Epoxy-MSiO$_2$ nanoparticles, peak-differentiation-imitating analysis was carried out, as shown in Figure 2e,f. C 1s peak was clearly divided into three peak components with the BE of 288.6, 286.2, and 284.7 eV, corresponding to carboxyl carbon (C=O), methyl side ether carbon (C-O), and carbon-hydrogen carbon (C-C/H) (Tables S-3 and S-4, Figure S-4), respectively. In addition, the high resolution of Si 2p spectra was consistent with two silica environments owning to BE at 103.8 and 102.9 eV, which was assigned to O—Si—O and O—Si—C species (Table S-5, Figure S-5). These facts further corroborated that PMMA long chains had been positively covalently bonded onto the exterior surface of SiO$_2$.

Further characterizations such as $^{29}$Si NMR (Figure S-6), TGA (Figure S-7), TEM (Figure S-8) and DSC (Figure S-9) were performed and listed in Table 1. From TEM data, the finely improved dispersion and gradually formed gray corona for both nanoparticles ($d = 16 \text{ nm}/110 \text{ nm}$) were clearly observed, after being modified with epoxide groups and PMMA long chains successively. On the basis of the TGA data, the grafting density ($\sigma_{\text{Epoxy-MSiO}_2}$) was calculated to be 0.27 chain/nm$^2$ for Epoxy-MSiO$_2$ ($f_{\text{SiO}_2} = 74.5 \text{ wt } \%$) and 3.1 chains/nm$^2$ for LEpoxy-MSiO$_2$ ($f_{\text{SiO}_2} = 63.0 \text{ wt } \%$), respectively, which was in agreement with the previous study in which the nanoparticles containing higher surface area were conducive to the accommodation of more grafts. In addition, an obvious elevation of $T_g$ of PMMA chains ($T_g, \text{Epoxy-SiO}_2 = 139.9 \degree C$, $T_g, \text{PMMA-COOH} = 91.5 \degree C$) was acquired from the DSC technique. It was directly
related to the immobilization effect of PMMA onto the solid inorganic core. The mobility of PMMA chains was confined, and the free volume decreased significantly. Similar results (Figures S-10 and S-11) were obtained for the nanoparticles with larger inorganic core ($d_{\text{SiO}_2} = 110$ nm). These facts above indicated that the "step-by-step" modifications of SiO$_2$ took place and the reactive epoxide groups as well as long PMMA chains have been successfully attached onto the surface of SiO$_2$.

3.1.3. Estimation of Reactivity of Epoxy-MSiO$_2$: In Situ Coupling Reaction during Blending. The reactivity of Epoxy-MSiO$_2$ is a key factor for the following reaction with the PLLA molecular chains so that Epoxy-MSiO$_2$ enhances the interfacial interaction between polymer components during the reactive compatibilizing process. As demonstrated in our previous study,$^{4,8,15,17}$ an in situ coupling reaction between epoxide and carboxyl groups could be envisaged during melt blending, facilitating the compatibilizing efficiency of immiscible polymer pairs. In this section, the reaction between PLLA and Epoxy-MSiO$_2$ was first conducted, under the same melt processing condition, to verify the feasibility of this methodology applied to
reactive compatibilization. As shown in Scheme 2, a cycloaddition reaction between the remaining epoxide groups of Epoxy-MSiO2 and terminating carboxyl groups of PLLA occurred. Double long chains grafted nanoparticles containing both pregrafted PMMA tails and in situ grafted PLLA chains were obtained. Note that the grafting of both PMMA and PLLA is random and the analysis in the real compatibilization will be discussed in the following section. The reactants after the melt blending, termed as LM-SiO2 (PMMA-random-PLLA)-g-SiO2, were separated from the mixture with unreacted PLLA components by repeated suspension (chloroform), centrifugation, and decanting of the supernatant.

The obtained LM-SiO2 was verified by the FT-IR in Figure 3a. Compared with Epoxy-MSiO2, the spectra of LM-SiO2 presented a shoulder peak around 1730 cm⁻¹, assigned to the characteristic peak of carboxyl groups. The selected band in Figure 3a was enlarged in Figure 3b. The peak could be curve-fitted with two band segments with the wavenumber at 1723 cm⁻¹ (PMMA) and 1757 cm⁻¹ (PLLA), indicating that both PLLA grafts and PMMA tails were presented on the surface of SiO2 nanoparticles. The ratio of I₁₇₂₃/I₁₇₅₇ (intensity of peak) could be applied to verify the weight composition of PLLA and PMMA. On the basis of the normalized curves (Figure S-12), the weight composition of PLLA tails was estimated to be 51.3 wt %. The presence of PLLA grafts was also verified by TGA, evident from the significantly reduced weight loss (f_LM-SiO2 = 61.9 wt %, f_Epoxy-MSiO2 = 75.2 wt %) and broadened differential peaks as shown in Figure 3c,d. Moreover, the appearance of Tg around 58.4 °C (attributed to PLLA chains) was observed from DSC, consistent with the previous results (Figure S-13).

Thereby, Epoxy-MSiO2 particles show high reactivity after grafting with PMMA and can be further melt grafted by PLLA molecular chains. In the following section, Epoxy-MSiO2 would be utilized as a new type interfacial compatibilizer in the well-characterized immiscible PVDF/PLLA (50/50, w/w) blends by reactive melt blending.

3.2. Reactive Compatibilization of Epoxy-MSiO2 for PVDF/PLLA Blends. 3.2.1. Localization of SiO2 and Epoxy-SiO2. To allow a meaningful appraisal of the performance of Epoxy-MSiO2 i.e., a beadlike emulsifier, the PVDF/PLLA (50/50, w/w) blends with pristine SiO2 and Epoxy-SiO2 were investigated for comparison. First, 1 wt % of SiO2 was incorporated into the 50/50 blend by melt compounding to estimate the selective dispersion of pristine SiO2. As shown in Figure 4a1, the blend displayed a typical feature of sea-island morphology with a broad distribution of PVDF-domain size (8.9 ± 9.6 μm), indicating a strong incompatibility and high interfacial tension between PVDF and PLLA phases. The enlarged SEM micrographs (Figure 4a2) demonstrated that the SiO2 nanoparticles were aggregated and located almost entirely in the PLLA matrix with little interfacial accommodation. Similar results were obtained for PVDF/PLLA blends with LSiO2 (Figure S-14). The surface modification of pristine SiO2 from OH groups into epoxide groups does not change the location of the nanoparticles in the blend. As shown in Figure 4b,b2, all the Epoxy-SiO2 particles are selectively located in the PLLA phase and PLLA/PVDF blends show almost the same phase structure with incorporation of pristine SiO2 or Epoxy-SiO2.

The selective location of SiO2 and Epoxy-SiO2 within the PLLA matrix was further confirmed to be stable against kinetic interruptions such as shear fields and high temperature annealing. It could be concluded that the thermodynamic equilibrium position of SiO2/Epoxy-SiO2 was supposed to be the PLLA phase, which would be discussed more detail later.

3.2.2. Localization of in Situ Formed Janus Silica Nanoparticles (JSNp): Effect of Particle Size. To further investigate the influence of PMMA grafts on the location of SiO2 as well as the resultant morphology of blends, two kinds of Epoxy-MSiO2 with different SiO2 sizes were utilized and added into the PVDF/PLLA (50/50, w/w) blends by the same strategy. Interestingly, both Epoxy-MSiO2 and LEpoxy-MSiO2 were found to be jammed exclusively at the PVDF/PLLA interface, which was totally different from the observations of pristine SiO2 and Epoxy-SiO2 above, as shown in Figure 5. We also noticed that the interface turned better adhesion, suggesting the ability of Epoxy-MSiO2 to improve interfacial adhesion (Figures S-15 and S-16). Presumably, Epoxy-MSiO2 could modify the morphology when preferentially located at the interface and serve as a true emulsifier for the typical immiscible PVDF/PLLA blends.

As compared with the blends containing LEpoxy-MSiO2, PVDF domains of the blends with Epoxy-MSiO2 exhibited more uniform distribution and better dispersion (Figure 5b), signifying more efficient compatibilizing ability of Epoxy-MSiO2. It was in
agreement with a previous study: Ginzbur et al.\textsuperscript{59} reported that the very small particles ($R_y < R_g \sim 15 \text{ nm}$) could influence the configuration entropy of its exterior polymer chains and functioned as compatibilizer effectively. On the basis of the results, Epoxy-MSiO$_2$ (finer particle) was selected to further investigate the effect of loadings on compatibilization in the next section.

**3.2.3. Epoxy-MSiO$_2$ Loading Effects on the Morphologies and Properties of the Blends.** To utilize the new concept above and estimate the effect of Epoxy-MSiO$_2$ on compatibilization, five blends of PVDF/PLLA (50/50, w/w) were fabricated by varying Epoxy-MSiO$_2$ loadings from 0 to 5 wt %. In the absence of Epoxy-MSiO$_2$, typical sea-island morphology formed with irregular PVDF domains of $10.1 \pm 12.3 \text{ \mu m}$ in PLLA matrix (Figure 6a). Besides, the PVDF/PLLA interface was clearly apparent with many cavities (Figure 6a), indicating poor adhesion between phases, as reported in our previous study.$^{14,15}$

Upon the addition of Epoxy-MSiO$_2$ into blends, the morphology exhibited a considerable reduction in the domain size, as depicted in Figure 6b,c,d,e. On the other hand, it should be noticed that all of the nanoparticles were located exclusively at the PVDF/PLLA interface, regardless of Epoxy-MSiO$_2$ content (Figure 6b,c,d,e). This indicates the thermodynamic compatibilization effects of the functionalized nanoparticles.

TEM observation (Figure 7) was performed to get a better overview of the interfacial coverage for nanoparticles. Here, the white phase, gray phase, and black dots referred to PLLA matrix, PVDF domain, and hybrid nanoparticles, respectively. Nanoparticles located selectively at the PVDF/PLLA interface, which was consistent with the SEM micrographs above. It is difficult to distinguish the asymmetric structure of the interfacial nanoparticles since both PLLA and PMMA grafts consist of the same C, H, and O elements. However, an analogous Janus-shell nanoparticle is observed at the PVDF/PLLA interface, as shown in Figure 7d. It provides a direct evidence of the formation of Janus nanoparticles.

Figure 8 shows the statistical analysis of PVDF-domain sizes and the thickness of the interfacial layer as a function of the particle loadings. It is seen from Figure 8a that the domain size linearly reduced with the increasing concentration of Epoxy-MSiO$_2$ in the blends ranging from 0.5 to 3 wt %. At 3 wt % of Epoxy-MSiO$_2$, the domain diameter decreased by about 5-fold over the corresponding pristine blends to $1.9 \pm 0.7 \text{ \mu m}$. A finer and more uniform PVDF domain was obtained with higher Epoxy-MSiO$_2$ loadings (5 wt %), which was quite different from previous studies\textsuperscript{20−22} demonstrating that only a fraction (∼3 wt %) of compatibilizer seemed to be enough to saturate the interface. Furthermore, as estimated in Figure 8b, the thickness of interfacial layer, surrounded with silica nanoparticles, increased from 50 nm at 0.5 wt % to 58.0 nm at 1 wt %. Then, the thickness remained constant with further increasing Epoxy-MSiO$_2$ loadings (from 3 to 5 wt %). Previous studies have confirmed that the desorption energy of a singular corona particle was three times lower than the Janus one. Due to the combination of rigid SiO$_2$ core and higher desorption energy of Janus-grafted corona, the in situ formed Janus silica nanoparticles (JSNp) (discussed later) were thermodynamically stable at the PVDF/PLLA interface against the shear field and the high processing temperature. Thus, high loading of Epoxy-MSiO$_2$ resulted in the accommodation of the PVDF/PLLA interface with much more interfacial area, facilitating the significant reduction of domain size, which was consistent with the morphology observations.

The fact that both the JSNp locates exclusively at the interface and the JSNp thickness stays almost constant indicated the good correlation between the dispersion phase size and the reactive nanoparticles loadings. In other words, higher loading of Epoxy-MSiO$_2$ leads to the larger interface area and the smaller domain size. This provides the facile strategy to design the morphology of the JSNp compatibilized immiscible polymer blends by incorporation of various amounts of reactive nanoparticles.

The thermodynamic properties were measured as a function of temperature to explore the change of compatibility and storage modulus with the addition of Epoxy-MSiO$_2$ in blends. As illustrated in Figure 9a, with the increase of Epoxy-MSiO$_2$, the glass transition temperatures ($T_g$) of both PVDF and PLLA shifted toward each other gradually, indicating enhanced miscibility between phases. Details of the parameters were listed.

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Figure 6. SEM images of PVDF/PLLA (50/50) blends illustrating the change in PVDF-domain size and distribution of nanoparticles with various Epoxy-MSiO$_2$ loadings (wt %): (a) 0, (b) 0.5, (c) 1, (d) 3, and (e) 5.
in Table S-6. Besides, the recovery of storage modulus ($E'$) values in the temperature range of 65–115 °C, corresponding to the cold crystallization of PLLA, increased with the addition of Epoxy-MSiO$_2$. This means that the Epoxy-MSiO$_2$-incorporated blends could be self-supported even above the $T_g$ of PLLA, which was related to the enhancement of interfacial interactions by increasing nanoparticles. Notably, such interfacial jammed nanoparticles were in favor of transferring stress under external

Figure 7. TEM images of PVDF/PLLA (50/50) blends demonstrating interfacial encapsulation with various Epoxy-MSiO$_2$ loadings (wt %): (a) 0, (b) 0.5, (c) 1, (d) 3, and (e, f) 5 wt %. The interfacial black dots are the resultant JSNp.

Figure 8. (a) Average size of PVDF domains (measured from SEM images) and (b) calculated Epoxy-MSiO$_2$ coating thickness at the PVDF–PLLA interface (measured from TEM images) as a function of the Epoxy-MSiO$_2$ loadings.

Figure 9. (a) Loss tangent and (b) storage modulus as a function of temperature with a frequency of 5 Hz for PVDF/PLLA (50/50, w/w) blends with various concentration of Epoxy-MSiO$_2$, obtained by dynamic thermomechanical analysis (DMA).
force due to the improved interfacial interactions between phases (Figure S-17). It should also be noted that the mechanical properties of the blends (both PLLA/PVDF (50/50) and (35/65)) increase greatly with the addition of the compatibilizers, as compared to those blends without compatibilizers (Tables S-7 and S-8, Figures S-18 to S-20). For example, the elongation at break and the tensile strength for the compatibilized blend are 10.7% and 56.0 MPa, while those for the uncompatibilized are 5.7% and 43.5 MPa, respectively.

4. DISCUSSION

4.1. Compatibilizing Mechanism of JSNp through Reactive Blending. From the results above, we demonstrate a novel strategy, termed as IPC mechanism, to emulsify the immiscible binary polymer blends by packing nanoparticles thermodynamically and exclusively at the polymer–polymer interface via reactive blending. As shown in Scheme 3, a new kind of reactive hybrid nanoparticle, Epoxy-MSiO₂, was synthesized through the “attaching onto” approach first (Section 3.1.1). Such nanoparticle containing both reactive epoxide groups and long PMMA chains on a solid SiO₂ core can further react with PLLA during melt compounding (Section 3.1.2). Epoxy-MSiO₂ was then employed as interfacial modifier to compatibilize the immiscible PVDF/PLLA blend. Since the SiO₂ core preferred to locate in PLLA matrix (Section 3.2.1) by thermodynamic force while the PMMA long tails exhibited better compatibility with PVDF phase, Epoxy-MSiO₂ was forced to anchor the interface in the initial stage of melt compounding before the in situ reaction. As the reaction between epoxide groups of Epoxy-MSiO₂ and terminated carboxyl groups of PLLA occurred, two kinds of polymers attached randomly to the exterior surface of SiO₂ by chemical bonds successively to form heterogeneous polymer corona (Section 3.1.3). Due to the strong immiscibility between PLLA and PMMA grafts, the exterior surface of SiO₂ turned into a Janus PMMA/PLLA corona spontaneously across the interface (Figure 7d). We redefine the in situ formed interfacial nanoparticles as Janus silica nanoparticles (JSNp) to distinguish them from original LM-SiO₂ with random distribution of PMMA/PLLA grafts. The JSNp featured a solid SiO₂ core and equally weighted PMMA/PLLA hemispheres. On the one hand, JSNp stretched its hemispheres, respectively, promoting the in situ formed PLLA tails (long PMMA chains) to interact with PLLA (PVDF) phase for maximizing energetically favorable contacts. On the other hand, the solid silica-core served as stiff nanofiller to improve interfacial stability. Therefore, the interfacial JSNp, which built up a dense layer around PVDF domains, could reinforce interfacial adhesions and effectively facilitate the compatibilization effect. Next, we paid close attention to the thermodynamic theory on the morphology evolution.

4.2. Thermodynamic Prediction of Silica Location with Various Surface Chemistries. Given the significant compatibilization effects by interfacial JSNp, it is desirable to acquire a thermodynamic approach to predict the location of silica nanoparticles with various surface chemistries. Herein, the location of SiO₂ in PVDF/PLLA blends can be estimated by evaluating wetting parameter \( \omega \) using Young’s model⁶⁰,⁶¹,⁴⁸ (eq 3):

\[
\omega = \frac{\gamma_{\text{SiO}_2-\text{PVDF}} - \gamma_{\text{SiO}_2-\text{PLLA}}}{\gamma_{\text{PVDF-PLLA}}}
\]

Here, \( \gamma \) represented the interfacial energy of the interfaces within blends: the SiO₂–PVDF interface, the SiO₂–PLLA interface, and the PVDF/PLLA interface. Different cases occurred: when \( \omega > 1 \), SiO₂ was expected to be located in the PLLA matrix; when \( \omega < -1 \), SiO₂ preferred to be positioned in the PVDF domains. Only when \( -1 < \omega < 1 \), SiO₂ would be thermodynamically preferred to jam at the PVDF/PLLA interface.

Owing to the difficulty in precisely estimating the interfacial energies, they were usually evaluated by the known surface energies of each component using the geometric (eq 4)⁶⁰,⁶¹,⁴⁸ or harmonic mean equations⁶⁰,⁶¹,⁴⁸ (eq 5):

\[
\chi_{ij} = \gamma_i + \gamma_j - 2 \sqrt{\gamma_i \gamma_j}
\]

\[
\chi_{ij} = \gamma_i + \gamma_j - \frac{4 \gamma_i \gamma_j}{\gamma_i^{d} + \gamma_j^{d}}
\]

Here, \( \gamma \) referred to the surface energy and \( \gamma^{d} \) and \( \gamma^{p} \) denoted the dispersive and polar contributions of the surface energies of components, respectively (\( \gamma = \gamma^{d} + \gamma^{p} \)). The values of surface energy of each component at processing temperature have been
acquired from the literature and listed in Tables S-9 and S-10.

As shown, the interfacial tensions of PVDF-SiO$_2$ and PLLA-SiO$_2$ were calculated to be 6.21 and 4.4 mJ m$^{-2}$ (eq 4) or 11.7 and 8.04 mJ m$^{-2}$ (eq 5). Thus, Young’s model (eq 3) resulted in a wetting parameter of 9.53 or 8.31, implying that SiO$_2$ should be preferentially positioned in PLLA matrix, which was in agreement with the results above (Figure 4). Also, the surface modification of pristine SiO$_2$ from hydroxyl groups to epoxy groups does not change the location as shown in Figure 4b, which was attributed to the improved affinity between SiO$_2$ and PLLA phase as a result of in situ grafting reaction of PLLA chains onto the surface of SiO$_2$.

With the incorporation of both long PMMA chains and epoxy groups onto SiO$_2$, the location differed. Since there are no accurate data available from the literature for the modified SiO$_2$ (Epoxy-MSiO$_2$) with the two polymers, we cannot provide the quantitative $\gamma_{\text{Epoxy-MSiO}_2}$-Polymer values. However, some qualitative analysis could be performed to provide an evaluation of interfacial tension trends. As calculated in Table S-9, the PVDF-PMMA pair showed the best compatibility ($\gamma_{\text{PVDF-PMMA}} = 0.025$ mJ m$^{-2}$) among all binary pairs and seemed totally miscible during blends. Besides, the SiO$_2$-PLLA interfacial energy was less than that of SiO$_2$-PMMA or SiO$_2$-PVDF, which caused the thermodynamic equilibrium of SiO$_2$ in the PLLA phase. Assuming that the kinetic disruptions were negligible, since all blends were prepared simultaneously above the melting point (190 °C) with sufficient time (10 min), nanoparticles were able to achieve equilibrium state. We speculate that, in the initial stage of blending, PMMA grafts were able to adjust their shell structure through selectively stretching toward the PVDF phase, which was beneficial for enthalpically favorable interactions. Meanwhile, the SiO$_2$ core preferred to be located in the PLLA matrix via thermodynamic prediction. Thus, Epoxy-MSiO$_2$ particles were forced to be jammed at the PVDF/PLLA interface since PMMA long tails were linked with SiO$_2$ by chemical bond before the in situ reaction occurred. As the reaction takes place, the second grafts, PLLA chains, were attached randomly onto the exterior of SiO$_2$. In order to maximize the contacts between grafts and blends, the nanoparticles took on Janus-corona configuration, facilitating PMMA tails (PLLA grafts) to interact with PVDF (PLLA phase), respectively. Of note, Müller and co-workers confirmed that the desorption energy of singular corona particle was three times lower than the Janus one. Therefore, JSNp “arrested” the interface and prevented it from coalescence.

Figure 10 shows the SEM images for the compatibilized sample after being statically annealed at 200 °C for 20 min. It is clear that the phase morphology of the blend was preserved and all nanoparticles were jammed at the PVDF/PLLA interface, as the sample before annealing in Figure 6d, indicating the very stable structure of the compatibilized blends. This is attributed to both the compatibilizing effects of the nanoparticles and the rigid inorganic core. It is considered that the nanoparticles are rheologically difficult to be pulled out of the interface against the annealing and the mechanical shearing, as compared with the traditional block/graft copolymer compatibilizers.

5. CONCLUSION

We demonstrated a novel approach, termed as IPC mechanism, to compatibilize the immiscible PVDF/PLLA blends by packing nanoparticles thermodynamically and exclusively at the interface through melt reactive blending. First, the reactive SiO$_2$ with both reactive epoxy groups and PMMA long chains, called Epoxy-MSiO$_2$, was synthesized by the “attaching onto” approach. The Epoxy-MSiO$_2$ showed high reactivity and could be covalently grafted with PLLA by in situ ring-opening reaction during blending. Despite the random distribution of grafts, the hybrid nanoparticles spontaneously formed into a Janus PMMA/PLLA corona across the PVDF/PLLA interface due to the specific interactions of the PMMA grafts with PVDF chains and PLLA grafts with PLLA chains. In order to maximize an energetically favorable interaction, the pregrafted PMMA tails and the in situ grafted PLLA chains on the SiO$_2$ core simultaneously adjusted their configuration by interacting selectively toward the miscible components. In addition, the solid nanoparticle core of the final Janus PMMA/PLLA nanoparticles could further take on the role as stiff nanofiller to enhance interfacial stability. The combination of steric repulsion by stiff silica core and strong interfacial affinity originated from selective molecular entanglements promoting the abundant adsorption of nanoparticles to the PVDF/PLLA interface irrespective of the severe processing conditions. The IPC paves a new possibility for the compatibilization of immiscible polymer blends. Moreover, a similar strategy might also be applied for the various types of nanoparticles used as both effective compatibilizer and functional fillers for multiphase polymer materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b01728.

Additional data for reaction equation of telomerization (Scheme S-1), molecular parameter of PMMA-COOH (Table S-1), XPS parameters of SiO$_2$ (Table S-2), $\bar{C}$ spectrum for Epoxy-SiO$_2$ (Table S-3), $\bar{C}$ is parameters for Epoxy-MSiO$_2$ (Table S-4), Si 2p parameters for Epoxy-MSiO$_2$ (Table S-5), thermal parameters from DMA (Table S-6), mechanical properties of PVDF/PLLA (50/50) blends (Table S-7), mechanical properties of PVDF/PLLA (65/35) blends (Table S-8), surface energy of polymer–particles (Table S-9), particle location in the blends (Table S-10), $^1$H NMR spectrum of PMMA-COOH (Figure S-1), FT-IR spectrum of PMMA-COOH (Figure S-2), GPC curve of PMMA-COOH (Figure S-3), $^1$H spectrum of Epoxy-SiO$_2$ (Figure S-4), Si 2p spectrum of Epoxy-MSiO$_2$ (Figure S-5), $^29$Si NMR spectrum (Figure S-6), TGA curves of SiO$_2$ (Figure S-7), TEM images of SiO$_2$ (Figure S-8), DSC curves of PMMA-COOH and Epoxy-MSiO$_2$ (Figure S-9), TGA curves of
LSiO₂ (Figure S-10), TEM images of LSiO₂ (Figure S-11), fitted carboxyl spectra of LM-SiO₂ from FT-IR (Figure S-12), DSC curves of Epoxy-MSiO₂ and LM-SiO₂ (Figure 13), SEM image of PVDF/PLLA (50/50) blends (Figure S-14), topography images of PVDF/PLLA (50/50) blends (Figure S-15), AFM topography of PVDF/PLLA (50/50) blends (Figure S-16), tensile specimen of PVDF/PLLA (50/50) blends (Figure S-17), tensile curves of PVDF/PLLA (50/50) blends (Figure S-18), tensile curves of PVDF/PLLA (65/35) blends (Figure S-19), SEM images of PVDF/PLLA (65/35) blends (Figure S-20) (PDF)

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**Notes**

The authors declare no competing financial interest.

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