Compatibilization Behavior of Double Spherical TETA–SiO2@PDVB Janus Particles Anchored at the Phase Interface of Acrylic Resin/Epoxy Resin (AR/EP) Polymer Blends

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ABSTRACT: The inorganic particles used as a compatibilizer play a role in crack termination and heat resistance. However, the poor compatibility of inorganic particles and polymer hinders their application. Herein, the double spherical SiO2@PDVB Janus particles (JPs) were modified with triethylene-tetramine (TETA), and the obtained anisotropic TETA–SiO2@PDVB JPs were used as the compatibilizer of acrylic resin/epoxy resin (AR/EP) composites. The modification and the compatibilization of TETA–SiO2@PDVB JPs were studied by scanning electron microscopy, X-ray photoelectron spectroscopy, differential scanning calorimetry, and dynamic mechanical analyzer, impact test, tensile test, and so forth.

Results show that amino groups grafted onto the SiO2 lobe can react with epoxy groups of EP, which results in the TETA–SiO2 lobe being embedded in the EP phase and the PDVB lobe being pushed toward the AR phase. The TETA–SiO2@PDVB JPs anchored at the interface of AR and EP increase their interfacial adhesion, decrease the domain phase size and distribution of dispersed AR, and improve the compatibility of AR/EP composites. The compatibilization of nanoparticles (NPs) is realized by the cavitation and blunting of different scaled AR phase domain distributions and that of JPs is realized by the strong interfacial force originated by JPs. Moreover, the desorption energy of TETA–SiO2@PDVB JPs is higher than that of SiO2–TETA; so the glass transition temperature (Tg) of AR/EP/JP composites is higher than that of AR/EP/NP composites. The strong interfacial adhesion and high desorption energy endow TETA–SiO2@PDVB JPs with a toughening effect and enhancing effect. The impact strength and the tensile strength of AR/EP/TETA–SiO2@PDVB composites are 16.03 kJ/m2 and 63.12 MPa, which are 9.91 kJ/m2 and 16.32 MPa higher than those of AR/EP/NP composites, respectively. JPs used in the thermosetting EP is beneficial to its toughening study and the new anisotropic Janus compatibilizer.

1. INTRODUCTION

Polymer blending is a simple and efficient way to obtain a kind of material with desirable properties. It is also an energy-saving and economical production method in the industry. However, the incompatibility of polymers inhibits the combination of excellent properties of blends. Therefore, improving blend compatibility is very crucial and becomes a research focus. Traditionally, efforts have been focused on the improvement of the morphological behavior of such blends via the incorporation of compatibilizing phases, which are either miscible or can chemically react with both blend components.† There are many compatibilizers available such as reactive polymers,2,3 organic copolymers (block, random, or grafted),4–6 nanomaterials (NPs),7 so forth. NPs can reduce the interfacial tension because of their surface effect. Inorganic NPs can also be used as compatibilizers because they tend to bridge immiscible polymers and offer their own intrinsic functionalities.8 The SiO2 NPs with high surface energy and adsorption capacity is nontoxic and nonpolluting. The surface of SiO2 NPs contains active hydroxyl groups, which can be physically entangled or chemically reacted with composite materials.9,10 As an environmental friendly inherent nanofiller, SiO2 NPs without functional modification are often used as fillers or coatings for toughening and materials with aging resistance or abrasion resistance. The functionalized SiO2 NPs have wider applications, such as printing binder,12 drug carrier,13 pigment (dyed),14 antibacterial materials,15 compatibilizer,16 and so on. Zhang16 studied the compatibilization of PP/polystyrene (PS) with SiO2 NPs and found that PP/PS blend compatibility could be dramatically improved with the addition of SiO2 NPs containing a large number of alkyls in their surface. The functionalized SiO2 NPs possessed more efficient compatibilization than unmodified SiO2 NPs. Anisotropic Janus particles (JPs) have higher interfacial activity, higher interfacial desorption energy, and lower surface tension than isotropic...
NPs. The JPs with two faces can be adsorbed strongly at interfaces, stronger than homogeneous NPs.\(^{19-21}\) Besides, the combination of amphiphilicity and particulate character (Pickering effect) favors strong and selective adsorption to interfaces because the chemical property of either face is similar with one phase of blends.\(^{21}\) JPs are compartmentalized colloids which possess two sides of different chemistries or polarities.\(^{23,24}\) These particles have broad potential applications in solid surfactants, oil and water separation,\(^{25,26}\) optical probes and E-paper display technology,\(^{27}\) and compatibilizers.\(^{20,28}\) Nie\(^{29}\) synthesized a Janus nanosheet and evaluated its ability to trap nonequilibrium morphology by interfacial self-assembly. The Janus nanosheet was synthesized by selectively grafting polymer chains, PS, or polyisoprene (PI) on each side of a silica nanosheet. The selective grafting endowed the nanosheet with two different wettabilities, which made it possible to self-assemble and further jam at the PS/PI interface. The study showed that the interfacial jamming nanosheet could trap the intermediate, nonequilibrium morphology during phase separation of polymer blends. The Janus nanosheet had high interfacial activity and could reduce the free energy of blends more effectively.

Epoxy resins (EP) are widely used in areas such as coatings, adhesives, structural applications, and electronics because of their thermal and chemical resistance, superior electrical properties, relatively low shrinkage, and good adhesion to many substrates.\(^{30}\) However, as a thermosetting resin, the brittleness of EP limits its application.\(^{31}\) The common toughening method of EP is the introduction of the second phase into the EP matrix, which is used to absorb stress. Rubber elastomers, thermoplastic resins, and rigid particles are known as toughening agents for EP.\(^{32,33}\) Acrylic resin (AR) has excellent anti-impact properties of elastomers and perfect thermal stability of resins. It is quite different from EP toughened by rubber because AR is a polar material. The domain size of the AR-dispersed phase is small and uniform. However, this blending structure is not beneficial to transfer stress. It is important to increase the dispersity of domain size of the dispersed phase in order to play different roles of different scale particles.\(^{34}\)

Herein, the lobe of SiO\(_2\) in SiO\(_2\)@PDVB was modified with triethylenetetramine (TETA), and the obtained TETA–SiO\(_2\)@PDVB JPs were used as the compatibilizer of AR/EP composites. The effects of the dosage of TETA–SiO\(_2\)@PDVB JPs on the AR/EP phase behavior, glass transition temperature, and mechanical properties were investigated. The distribution and the location of TETA–SiO\(_2\)@PDVB JPs in AR/EP blends were also studied. The isotropic SiO\(_2\)--TETA NPs were compared with the anisotropic JPs.

### 2. RESULTS AND DISCUSSION

#### 2.1. Morphology of TETA–SiO\(_2\)@PDVB JPs. Figure 1\(a,b\) shows the scanning electron microscopy (SEM) photographs of unmodified and modified SiO\(_2\)@PDVB JPs. It shows that SiO\(_2\)@PDVB JPs are double spherical-like and have strict chemical compartmentalization between two lobes. The large lobe is organic PDVB and the small lobe is inorganic SiO\(_2\). The hydroxyl content of the SiO\(_2\) lobe increases after it is activated with HCl and H\(_2\)O\(_2\). In the presence of zeolite, dehydration reaction happens between the amino in TETA and the hydroxyl on the SiO\(_2\) lobe. The TETA chains are grafted onto the surface of the SiO\(_2\) lobe, and so the diameter of the TETA–SiO\(_2\) lobe increases by 34 nm (Figure 1\(c\)). At the same time, the long axis of TETA–SiO\(_2\)@PDVB JPs increases to about 614 nm from 580 nm of unmodified SiO\(_2\)@PDVB JPs.

#### 2.2. Chemical Composition of TETA–SiO\(_2\)@PDVB JPs.

Figure 2\(a\) shows the X-ray photoelectron spectroscopy (XPS) results of TETA–SiO\(_2\)@PDVB JPs. According to the binding energy lookup table for signals from elements and common chemical species, the chemical shift of Si 2p in SiO\(_2\) is 103.50 eV, while that of Si 2p in TETA–SiO\(_2\)@PDVB JPs moves to 102.93 eV. Because of the reaction of TETA and SiO\(_2\), the Si–O bond on the surface of the SiO\(_2\) lobe is replaced by the Si–N bond. The electronegativity of the N element is smaller than that of the O element, so the deshielding effect of the N element is less than that of the O element, which results in the decrease in the chemical shift. It is more important that the N 1s peak in 397.62 eV confirms the dehydration reaction between amino groups and hydroxyl groups. In addition, the methyl and methylene absorptive peaks in the IR spectrum

![Figure 1. Micrographs of (a) SiO\(_2\)@PDVB JPs, (b) TETA–SiO\(_2\)@PDVB JPs, and its (c) synthesis diagram.](image1)

![Figure 2. (a) XPS spectrum of TETA–SiO\(_2\)@PDVB JPs and (b) TGA curves of SiO\(_2\)@PDVB and TETA–SiO\(_2\)@PDVB JPs.](image2)
(support Figure 1) of SiO$_2$–TETA NPs show that there is no problem of reaction between TETA and SiO$_2$ lobes.

Figure 2b shows the thermograms of SiO$_2$@PDVB and TETA–SiO$_2$@PDVB JPs. The thermogravimetric curve of TETA–SiO$_2$@PDVB JPs is divided into two stages that are the degradation of the TETA onto the SiO$_2$ lobe and PDVB lobe. The starting decomposition temperature of TETA from TETA–SiO$_2$@PDVB JPs is 200 °C. Nitrogen release from the TETA decomposition helps extinguish the flame, that is to say, the TETA coated onto the surface of the SiO$_2$ lobe increases the modified JPs’s fire retardancy. As a result, the decomposition temperature of the PDVB lobe of TETA–SiO$_2$@PDVB JPs is higher than that of SiO$_2$@PDVB JPs.

2.3. Brittle Surfacial Morphology of AR/EP Composites. Figure 3 shows SEM images of the AR/EP composite brittle fracture surface. For AR/EP composites, the surface is very clear and the phase domain size of the AR dispersion is very uniform because they are both polar polymers (Figure 3a). In contrast, in the presence of unmodified SiO$_2$, the phase domain distribution of AR becomes broad and ranges from 0.18 to 3.5 μm (Figure 3b) because of the nano-effect of SiO$_2$. However, the unmodified SiO$_2$ NPs are apt to be coagulated in the EP matrix (red line area). Once the compatibilizer of SiO$_2$ NPs is replaced by SiO$_2$–TETA NPs, the phase domain distribution of AR becomes broader than that of SiO$_2$ NPs and ranges from 0.14 to 4.5 μm (Figure 3c) because of the reaction of amino groups in SiO$_2$–TETA NPs and the epoxy groups in EP. It is more important that the modified SiO$_2$–TETA NPs are located at the interface of AR and EP. No aggregations of SiO$_2$–TETA NPs are observed in the EP matrix. It is very interesting that the AR-dispersed phase size becomes small and nonuniform when JP compatibilizers are used (Figure 3d,e). There are two different points in AR/EP/SiO$_2$@PDVB composites and AR/EP/TETA–SiO$_2$@PDVB composites. In AR/EP/SiO$_2$@PDVB composites, the interface of AR and EP is distinct and the JPs protrude on the fracture surface. The outlines of JPs are very clear. There is no chemical bond action between JPs and AR, and so JPs are not at the interface of AR and EP. However, in AR/EP/TETA–SiO$_2$@PDVB composites, the TETA–SiO$_2$ lobe is embedded in the EP matrix and the PDVB lobe is pushed toward the AR area, and the neck of TETA–SiO$_2$@PDVB JPs is anchored at the interface of AR and EP. The interaction force between TETA–SiO$_2$@PDVB JPs and blends mainly comes from the chemical bond between amino groups and epoxy groups. In order to improve the compatibility and toughness of the composites, the rigid SiO$_2$ lobe is modified. SiO$_2$–TETA NPs are taken as an example of the size effect of the SiO$_2$–TETA lobe on the composite’s morphology. This is the effect of the ratio of two JP lobes.

2.4. Effect of SiO$_2$ Size on AR/EP Composites. The effect of NP sizes on the compatibilization of AR/EP composites is shown in Figure 4. The amount of NPs is fixed in 2 wt %. Both SiO$_2$ NPs and SiO$_2$–TETA NPs of 100 nm SiO$_2$–TETA, (d) 100 nm SiO$_2$–TETA, (e) 300 nm SiO$_2$–TETA, and (f) 500 nm SiO$_2$–TETA.
than that of AR/EP/SiO₂ because of the chemical reaction of SiO₂−TETA NPs with EP. The compatibilization of NPs is also reflected in the wide-phase domain size of AR when the NP size is 100 nm. When the NP size increases to 300 and 500 nm, the AR phase size distribution is narrow in AR/EP.

Moreover, the integrated action of the small AR phase size and the big NP size results in that NPs are not located at the interface of AR and EP any more.

**2.5. Effect of NP and JP Contents on AR/EP Composites.** The effect of the dosage of NPs and JPs on
the phase domain size of the dispersed phase in AR/EP composites is shown in Figure 5. When 1 wt % of SiO2 NPs or SiO2−TETA NPs is added, the average AR phase domains size are 854 and 1215 nm, respectively (Figure 6a,b), but the phase domain size distribution of AR becomes wider by adding 1 wt % of SiO2−TETA NPs than 1 wt % of unmodified SiO2 NPs. When 2 wt % of SiO2 NPs or SiO2−TETA NPs is added, the phase domain size of AR decreases obviously and the phase domain size distribution becomes wide (Figure 7a,b). However, when 3 wt % of SiO2 NPs or SiO2−TETA NPs is added, the AR phase domains become dense. At the same time, its phase domain size and distribution become small. It is obvious that NPs can change the phase domain size and distribution of the dispersed phase. When the NP content is less than 2 wt %, it cannot play a good role in the annealing process of the solid surfactant. It is worth noting that more NPs can be found in the brittle fracture surface of AR/EP/SiO2−TETA than that of AR/EP/SiO2, attributing to the reaction of amino groups and epoxy groups. When 1 wt % of TETA−SiO2@PDVB JPs is added, the average phase domain size of AR decreases to 524 nm, which is much smaller than the NPs used (Figure 6c). As TETA−SiO2@PDVB JP content increases to 4 wt %, the phase domain size of AR remains unchanged and the phase domain distribution becomes narrow (Figure 7c). Glaser et al. found that bimetallic JPs led to a significant reduction of the oil/water interfacial tension as compared to similar uniform particles.33 Compared with isotropic NPs, JPs are more effective in reducing interfacial tension. Because of the different chemical structures of the two lobes of JPs, with the reaction of the TETA−SiO2 lobe with EP, the PDVB lobe turns to the AR phase automatically (Scheme 1). The TETA−SiO2@PDVB JPs orient at the AR/EP interface and add the interfacial adhesion of AR and EP. The TETA−SiO2@PDVB JPs anchored in the AR/EP interface can restrain the agglomeration of the AR-dispersed phase and the AR phase domain size is concentrated in 0.2−0.9 μm.

2.6. Effect of NPs and JPs on the Compatibility of AR/EP Composites. Table 1 shows the glass transition temperature (Tg) of AR/EP composites. Tg is an important parameter in polymer blending and is often used as a criterion for determining the compatibility of blends. It is difficult to make two phases completely compatible in polymer blending. Most polymer blending is partially compatible, that is, Tg values of two phases are close to each other. The Tg values of AR/EP composites are 162.5 and 65 °C corresponding to EP and AR. The Tg difference of EP and AR is 97.5 °C. When SiO2 NPs, SiO2−TETA NPs, or TETA−SiO2@PDVB JPs is used as the compatibilizer of AR/EP composites, the Tg difference of EP and AR is 85.5, 77.5, or 91.5 °C, respectively. Because of the compatibilization of SiO2 and SiO2−TETA, the Tg values of the AR phase and EP phase are close to each other gradually. However, the Tg difference of EP and AR increases on the contrary, in AR/EP/TETA−SiO2@PDVB. The reason is that the desorption energy of NPs is 20 times lower than that of JPs from the interface of an immiscible polymer blend.33 The high desorption energy of JPs prevents them from moving out of the interface of AR/EP. The movement of the EP chain segment becomes difficult, so the Tg of EP rises up obviously.

Figure 8a shows tan δ as a function of temperature measured by a dynamic mechanical analyzer (DMA), and its peak is taken as Tg. All of the samples show a short peak corresponding to the glass transition of the AR phase in 70 °C and a high peak corresponding to the glass transition of the EP phase. It is worth noting that AR/EP/SiO2−TETA composites show an α-relaxation peak and a β-relaxation peak. On the one hand, SiO2−TETA NPs reacted with EP originate secondary relaxation. On the other hand, SiO2−TETA NPs have compatibilization on AR/EP composites. Because of the high desorption energy, the Tg value of AR/EP/TETA−SiO2@PDVB is higher than that of AR/EP/SiO2−TETA. Loss modulus can also be used to characterize Tg. Figure 8b shows that the loss modulus values of the AR and EP are close to each other in the presence of NPs and JPs. This indicates that SiO2 NPs, SiO2−TETA NPs, and TETA−SiO2@PDVB JPs improve compatibility of AR and EP.

2.7. Mechanical Property of AR/EP Composites. Impact strength and tensile tests are performed to evaluate the toughening and reinforcing effects of the incorporated NPs and JPs. NPs and JPs can change the phase domain size and phase domain distribution and also improve the mechanical properties of AR/EP composites. The results are shown in Figure 9. The impact strength of AR/EP composites is 6.12 kJ/m2 (Figure 9a). They increase to 7.55, 10.98, 15.21 kJ/m2, respectively, when 2 wt % SiO2 NPs, SiO2−TETA NPs, and TETA−SiO2@PDVB are added. Owing to the anisotropic property of JPs, the impact strength of AR/EP composites with 3 wt % of TETA−SiO2@PDVB JPs becomes 16.03 kJ/m2, which is 32.2% higher than that of pure EP. The similar polar of AR and EP benefits their blending. However, the uniform dispersed phase is difficult to finish cavitating and blunting at the same time; so it is very important to broaden the AR phase domain distribution. If SiO2 NPs are added, the AR phase domain distribution becomes broad and SiO2 NPs can blunt the crack tip. However, the poor interfacial adhesion of SiO2 NPs induces stress concentration, which results in the decline of impact strength. Modified SiO2−TETA NPs can form a

| samples          | Tg (°C) of AR | Tg (°C) of EP | Tg difference (°C) |
|------------------|--------------|--------------|--------------------|
| AR/EP            | 65           | 162.5        | 97.5               |
| AR/EP/SiO2       | 75           | 160.5        | 85.5               |
| AR/EP/SiO2−TETA  | 72.5         | 150          | 77.5               |
| AR/EP/TETA−SiO2@PDVB | 68          | 159.5        | 91.5               |
covalent bond with EP, bridge, and pin the crack line. Therefore, the toughness of AR/EP/SiO2−TETA composites is higher than that of AR/EP/SiO2 composites. When TETA−SiO2@PDVB JPs added into AR/EP composites, the interface between AR and EP is blurred, and the compatibility of the two phases is obviously improved, so the impact strength is improved significantly. In addition, the rive effect of JPs anchored at the interface of AR and EP prevents crack propagation and transmits impact force effectively. This firm attachment at interfaces may lead to advanced stabilizing properties in dispersions and improves the toughness of composites. The agglomeration of access NPs and JPs will lead to the poor mechanical properties. Figure 9b shows the tensile test of AR/EP composites with different contents of NPs and JPs. Results show that the tensile strength of the AP/EP composites is 46.80 MPa. Both NPs and JPs can increase the tensile strength of AR/EP composites obviously. The difference is that the tensile strength of the AR/EP composite with isotropic NPs increases first and then decreases because of the agglomeration of NPs, especially unmodified SiO2 NPs. The tensile strength of AR/EP composites with anisotropic JPs increases most quickly among three solid particles and reaches 63.12 MPa because of the interaction between TETA−SiO2@PDVB JPs and AR/EP. However, unlike EP toughened by rubber, incorporation of NPs and JPs into the AR/EP composites can toughen AR/EP composites without sacrificing their stiffness.

3. CONCLUSIONS

The SiO2@PDVB JPs are modified with TETA, and the obtained anisotropic TETA−SiO2@PDVB JPs are used as the compatibilizer of AR/EP composites. TETA grafted onto the SiO2 lobe can react with epoxy groups of EP, which results in the TETA−SiO2 lobe being embedded in the EP phase and the PDVB lobe being pushed toward the AR phase. The TETA−SiO2@PDVB JPs anchored at the interface of AR and EP increase their interfacial adhesion, decrease the domain phase size and distribution of dispersed AR, and improve the compatibility of AR/EP composites. The compatibilization of NPs is realized by the cavitation and blunting of different scaled AR phase domain distributions and that of JPs is realized by the strong interfacial force originated by JPs. Moreover, the desorption energy of TETA−SiO2@PDVB JPs is higher than that of TETA−SiO2, and so the glass transition temperature (Tg) of AR/EP/JP composites is higher than that of AR/EP/NP composites. The strong interfacial adhesion and high desorption energy endow TETA−SiO2@PDVB JPs with a toughening effect and enhancing effect. The impact strength and the tensile strength of AR/EP/JP composites are 16.03 kJ/m² and 63.12 MPa, which are 9.91 kJ/m² and 16.32 MPa higher than those of AR/EP composites, respectively. JPs used in the thermosetting EP is benefit to its toughening study and the new anisotropic Janus compatibilizer.

4. EXPERIMENTAL SECTION

4.1. Materials. Bisphenol EP (E-44, epoxy value is 0.44) was purchased from Hangzhou Wuhuigang Glue Industry Co. Ltd. AR (Mw is 45 024, PDI is 1.59, and hydroxyl value is 0) was purchased from Shenzhen Jitian Chemical Industry Co. Ltd. TETA, 4,4′-diaminodiphenylmethane (DDM), 4 A zeolite, anhydrous ethanol, dimethylbenzene, hydrogen peroxide solution (H2O2, 30%), hydrochloric acid (HCl, 2 mol/L), sodium hydroxide, acetone, ammonia (28 wt %), and tetraethoxysilane (TEOS) were purchased from Sinopharm Chemical Reagent.

4.2. Synthesis of SiO2 NPs. Anhydrous ethanol (200 mL) and 15 mL of ammonia (28 wt %) were mixed in a 250 mL of flask under stirring at ambient temperatures for 1 h. Then, 6 mL of TEOS was added into the mixture of ethanol and ammonia. The reaction was lasted for 24 h. Finally, the product was centrifuged and washed with water and anhydrous ethanol several times. The SiO2 NPs with a diameter of 50−100 nm were obtained after freeze-drying. The SiO2 NPs with
different sizes could be obtained by changing the ratio of ethanol to water.

4.3. Synthesis of SiO$_2$@PDVB JPs. JPs were prepared by seed emulsion polymerization according to the literature.$^{24}$

4.4. Surface Modification of the SiO$_2$ Lobe in SiO$_2$@PDVB JPs. First, the surface of the SiO$_2$ lobe in SiO$_2$@PDVB JPs was activated by H$_2$O$_2$ and HCl. As a result, the content of activated silicon hydroxyl was 17.86 OH/nm$^2$, which was 36.41% higher than that of the original SiO$_2$@PDVB JPs. Then, 2.0 g of activated SiO$_2$@PDVB JPs was dispersed in 20.0 g of dimethylbenzene in 150 mL flask under ultrasonication. Then, 10.0 g of TETA and 2.5 g of 4 A zeolite were added. The flask was heated to 210 °C and maintained for 24 h. After JPs were washed with anhydrous ethanol and freeze-dried, the product of TETA–SiO$_2$@PDVB JPs was obtained. The SiO$_2$–TETA NPs were obtained by the same method.

4.5. Preparation of AR/EP Composites. The blends of AR/EP (10/100, w/w) containing 0, 1, 2, 3, or 4 wt % TETA–SiO$_2$@PDVB were mixed at a temperature of 120 °C for 3 h. Next, the cross-linking agent of EP (DDM, 25 wt % to EP) was added into the previous mixture. After being stirred for 3 min, the mixture was poured into a preheated mold. The mold was put into an oven of 120 °C for 2 h and then heated to 160 °C and maintained for 2 h. After the mold was cooled to room temperature, the composites of AR/EP/TETA–SiO$_2$@PDVB were gained. The AR/EP/SiO$_2$ and the AR/EP/TETA–SiO$_2$ as the control were obtained using the same method.

4.6. Characterization. The morphology of JPs and the brittle fracture surfaces of polymer blends were observed with a JSM-7500F scanning electron microscope (SEM, JEOL, Tokyo, Japan) after the scanned surfaces were vacuum-sputtered with platinum at an accelerating voltage of 5 kV. Fourier transform infrared (FT-IR) spectra of the unmodified and modified TETA–SiO$_2$@PDVB JPs were recorded on a Nicolet-5700 FTIR spectrometer (Thermo Nicolet, USA) using KBr pellets. The bonding energy was characterized by an X-ray photoelectron spectrometer (XPS, ESCALAB 250, VG Ltd., USA). The thermal gravimetric analyzer (TGA, TA Q50, USA) was utilized to analyze the thermostability of SiO$_2$@PDVB JPs and TETA–SiO$_2$@PDVB JPs and to determine the amount of TETA on SiO$_2$@PDVB JPs. Impact performance of AR/EP/SiO$_2$ and the AR/EP/TETA–SiO$_2$ was tested with an impact strength tester LLOYD LR5K Tester with a 5 kN load cell at a crosshead rate of 5 mm/min. Each result was collected as an average value of five samples.

ASSOCIATED CONTENT

Supporting Information

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FT-IR spectra of unmodified and modified SiO$_2$ NPs and SiO$_2$@PDVB JPs (PDF)

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Notes

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REFERENCES

(1) Jiang, S.; et al. Preparation of functionalized graphene by simultaneous reduction and surface modification and its polymethyl methacrylate composites through latex technology and melt blending. Chem. Eng. J. 2013, 226, 326–335.
(2) Brown, S. B. Reactive compatibilization of polymer blends. In Polymer Blends Handbook; Utracki, L. A., Ed.; Springer Netherlands: Dordrecht, 2003; pp 339–415.
(3) Xu, Y.; et al. Reactive compatibilization of polylactide/polypropylene blends. Ind. Eng. Chem. Res. 2015, 54, 6108–6114.
(4) Adeeji, A.; Lyu, S.; Macosko, C. W. Block copolymers in homopolymer blends: Interface vs Micelles. Macromolecules 2001, 34, 8663–8668.
(5) Noolandi, J.; Hong, K. M. Interfacial properties of immiscible homopolymer blends in the presence of block copolymers. Macromolecules 1982, 15, 482–492.
(6) Zhang, H.; et al. Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content. Acta Mater. 2006, 54, 1833–1842.
(7) Taguet, A.; Cassagnau, P.; Lopez-Cuesta, J.-M. Structuration, selective dispersion and compatibilizing effect of (nano) fillers in polymer blends. Prog. Polym. Sci. 2014, 39, 1526–1563.
(8) Fu, Z.; et al. Immiscible polymer blends compatibilised with reactive hybrid nanoparticles: Morphologies and properties. Polymer 2017, 132, 353–361.
(9) Zhou, H. J.; et al. Effects of reactive compatibilization on the performance of nano-silica filled polypropylene composites. J. Mater. Sci. 2006, 41, 5767–5770.
(10) Chen, J. H.; et al. A comparative study of nanosilica/poly(propylene) composites prepared by reactive compatibilization. Macromol. Chem. Phys. 2008, 209, 1826–1835.
(11) Lin, J.; et al. In-situ fabrication of halloysite nanotubes/silica nano hybrid and its application in unsaturated polyester resin. Appl. Surf. Sci. 2017, 407, 130–136.
(12) Gao, D.; et al. Preparation of epoxy-acrylate copolymer/nano-silica via Pickering emulsion polymerization and its application as printing binder. Appl. Surf. Sci. 2018, 435, 195–202.
(13) Nampi, P. P.; et al. High surface area sol-gel nano silica as a novel drug carrier substrate for sustained drug release. Mater. Res. Bull. 2012, 47, 1379–1384.
(14) Yuan, J.; et al. Organic pigment particles coated with colloidal nano-silica particles via layer-by-layer assembly. Chem. Mater. 2005, 17, 3587–3594.
(15) Miola, M.; et al. Silver nanocluster-silica composite antibacterial coatings for materials to be used in mobile telephones. Appl. Surf. Sci. 2014, 313, 107–115.
(16) Zhang, Q.; Yang, H.; Fu, Q. Kinetics-controlled compatibilization of immiscible polypropylene/poly styrene blends using nano-SiO$_2$ particles. Polymer 2004, 45, 1913–1922.
(17) Zhang, X.; Sun, M.; Chen, W. Synergistic effects of silica nanoparticles and reactive compatibilizer on the compatibilization of polystyrene/polyamide 6 blends. *Polym. Eng. Sci.* 2017, 57, 1301.

(18) Vrsaljko, D.; Macut, D.; Kovačević, V. Potential role of nanfillers as compatibilizers in immiscible PLA/LDPE blends. *J. Appl. Polym. Sci.* 2015, 132, 41414.

(19) Parpaite, T.; et al. Janus hybrid silica/polymer nanoparticles as effective compatibilizing agents for polystyrene/polyamide-6 melted blends. *Polymer* 2016, 90, 34–44.

(20) Wang, H.; et al. Reactive nanoparticles compatibilized immiscible polymer blends: Synthesis of reactive SiO$_2$ with long poly (methyl methacrylate) chains and the in situ formation of Janus SiO$_2$ nanoparticles anchored exclusively at the interface. *ACS Appl. Mater. Interfaces* 2017, 9, 14358–14370.

(21) Walther, A.; Kerstin, M.; Müller, A. H. E. Engineering nanostructured polymer blends with controlled nanoparticle location using Janus particles. *ACS Nano* 2008, 2, 1167–1178.

(22) Bahrami, R.; et al. The impact of Janus nanoparticles on the compatibilization of immiscible polymer blends under technologically relevant conditions. *ACS Nano* 2014, 8, 10048–10056.

(23) Glaser, N.; et al. Janus particles at liquid-liquid interfaces. *Langmuir* 2006, 22, 5227.

(24) Sun, Y.; et al. Robust reactive Janus composite particles of snowman shape. *Macromolecules* 2015, 48, 2715–2722.

(25) Liang, F.; et al. Janus colloids towards interfacial engineering. *Langmuir* 2016, 34, 4123–4131.

(26) Yang, H.-C.; et al. Janus membranes: Creating asymmetry for energy efficiency. *Adv. Mater.* 2018, 30, 1801495.

(27) Walther, A.; Müller, A. H. E. Janus particles: synthesis, self-assembly, physical properties, and applications. *Chem. Rev.* 2013, 113, 5194–5261.

(28) Jiang, S. *Janus Particle Synthesis, Self Assembly and Applications*; RSC Publishing, 2012.

(29) Nie, H.; Liang, X.; He, A. Enthalpy-enhanced Janus nanosheets for trapping nonequilibrium morphology of immiscible polymer blends. *Macromolecules* 2018, 51, 2615.

(30) Ma, C.; et al. Economical and environment-friendly synthesis of a novel hyperbranched poly(aminomethylphosphine oxide-amine) as co-curing agent for simultaneous improvement of fire safety, glass transition temperature and toughness of epoxy resins. *Chem. Eng. J.* 2017, 322, 618–631.

(31) Guan, L.-Z.; et al. Mechanical properties and fracture behaviors of epoxy composites with phase-separation formed liquid rubber and preformed powdered rubber nanoparticles: A comparative study. *Polym. Compos.* 2015, 36, 785–799.

(32) Nguyen, F. N.; Berg, J. C. Novel core–shell (dendrimer) epoxy tougheners: Processing and hot–wet performance. *Composites, Part A* 2008, 39, 1007–1011.

(33) Le, Q.-H.; et al. Structure-property relations of 55 nm particle-toughened epoxy. *Polymer* 2010, 51, 4867–4879.

(34) Xu, W.; et al. Study on the compatibilizing effect of Janus particles on liquid isoprene rubber/epoxy resin composite materials. *Ind. Eng. Chem. Res.* 2017, 56, 14060.

(35) Walther, A.; Müller, A. H. E. Janus particles: synthesis, self-assembly, physical properties, and applications. *Chem. Rev.* 2013, 113, 5194–5261.