Nano-SiO₂/PMMA-PU composite particles with core-shell structure via emulsion polymerization and their application in epoxy resin

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ABSTRACT: A novel method of nano-SiO₂/poly(methyl methacrylate)(PMMA)-polyurethane(PU) composite particles modifying epoxy resin is reported. The composite particles with the obvious core-shell structure were prepared by emulsion polymerization of PMMA and PU prepolymer on the surface of nano-SiO₂. The diameter of the composite particles was 50–100 nm with dark core SiO₂ (30–60 nm) and light shell polymer of PMMA and PU (20–30 nm); moreover, PU was well distributed in PMMA with about 10 nm diameter. After nano-SiO₂ was encapsulated by PMMA and PU, the Si content on the surface decreased rapidly to 2.08% and the N content introduced by PU was about 1.27%. The ratio of polymer to original nano-SiO₂ (f_p), the grafting ratio of polymer to original nano-SiO₂ (f_r) and the efficiency grafting ratio of polymer (f_e) were, respectively, about 116.7%, 104.4%, and 89.5%. The as-prepared composite particles were an effective toughness agent to modify epoxy resin, and the impact strength of the modified epoxy resin increased to 46.64 kJ m^{-2} from 19.12 kJ m^{-2} of the neat epoxy resin. This research may enrich the field of inorganic nanoparticles with important advances toward the modification for polymer composite materials. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41919.

INTRODUCTION

The modification of polymers using inorganic nanoparticles has recently become one of the most important directions for improving the physical and mechanical properties of polymer composite materials.[1–4] Owing to the special properties of the nanoparticles, such as small size effect and high surface activity, many researchers are using inorganic nanoparticles to modify epoxy resin.[5–10] The addition of these inorganic nanoparticles does not change the chemical properties of the blend such as glass transition temperature (T_g) and cured craftwork, only depending on the pure physical technology, so it is very favorable for the amount of inorganic nanoparticles to be chosen conveniently. In most cases, the specific surface area increases with the particles size decreasing, resulting in the possible agglomeration of nanoparticles, if no specific surface treatment is applied beforehand. Especially, nanoparticles with a high concentration, the aggregation can take place easily even though the surface of nanoparticles are treated with silane coupling agent,[11] so the fabrication of polymer nanocomposite material is hindered by the tendency of the nanofillers to form agglomerates.[12,13] The encapsulation of nanoparticles by monomer polymerization can introduce a polymer layer to the particles

surface. The encapsulating polymer will act as a barrier to prevent nanoparticle agglomeration again and the individual encapsulating layer will provide a designable interface in polymer composites filled with inorganic nanoparticles.[1] Heterogeneous polymerization, especially emulsion polymerization, provides an effective way and is by far the most frequently used technique,[14] which is capable of forming nanoparticles dispersed in continuous phase-like water for encapsulation purposes.[15]

In this contribution, the surface of nano-SiO₂ was firstly modified by the hydrolysis of γ-methacryloxypropyltrimethoxysilane(MPTMS) coupling agents to improve the compatibility of nano-SiO₂ with polymers because inorganic particles and polymer are usually hydrophilic and hydrophobic.[16–18] Owing to easy migration and poor compatibility with polymer, the low-molecular-weight emulsifier was replaced by the composite emulsifier of polymerizable surfactant SE-10 and nonionic emulsifier OP-10. The 50–100 nm nano-SiO₂/PMMA-PU composite particles with dark core SiO₂ (30–60 nm) and light shell polymer (20–30 nm) were prepared by the emulsion polymerization of MMA and PU prepolymer on the surface of nano-SiO₂. The as-prepared organic/inorganic composite particles exhibit the properties of both the organic and the inorganic

materials simultaneously; moreover, they also combine the advantages of the excellent elasticity of polyurethane and the good chemical resistance of PMMA. Owing to the weak interface between silicon layers and the epoxy matrix, leading to debonding of the layers when fractured,[19] the PU is also introduced to improve the interface compatibility of nanoparticles and epoxy resin matrix, because the NH group in the PU can react with the epoxy group of epoxy resin; moreover, the hard and soft units of which are easily controlled in the PU molecule and endow it with the good anti-impact property and low-temperature toughness. To the authors' best knowledge, this report is the first one to describe the fabrication of composite core-shell nanoparticles of nano-SiO$_2$, PMMA and PU and their modification for epoxy resin. The microstructure and encapsulation effect are researched by FTIR, TEM, XPS, TGA, and Soxhlet extraction experiments, and the results indicate that the surface of nano-SiO$_2$ is encapsulated well by PMMA and PU with the high grafting ratio to original SiO$_2$ (f_r) and efficiency grafting of PMMA and PU (f_e). The prepared composite particles are used to modify epoxy resin, and the good toughness effect can be obtained by controlling the ratio of composite particles to epoxy resin. Finally, the fracture surfaces of the neat and modified epoxy resin are investigated by SEM.

EXPERIMENTAL

Materials

Toluene-2,4-diisocyanate (TDI), polyether glycol (N220, industry grade), 2,2-bis(hydroxymethyl)propionic acid (DMPA), dibutyltin dilaurate (DBTDL) were used as the received from Chinese company. Methyl methacrylate (MMA) and hydroxypropylacrylate (HPA) purchased from Chinese company were firstly washed by 5% sodium hydroxide and then purified by vacuum distillation before use. γ-Methacryloxypropyltrimethoxysilane (MPTMS) was purchased from Jiangsu Chenguang Co. China without further purification. Nano-SiO$_2$ was purchased from Hongsheng Co. China. The polymerizable emulsifier of allyloxy nonylphenoxy propanol polyoxyethylene ether ammonium sulfate (SE-10) was supplied by Kodi Gas Chemical Industry Co., LTD China, and octane phenol polyoxyethylene (OP-10, CP) was purchased from Baishi Chemical Engineer Co. China. Ammonium persulfate (APS) purchased from Lingfeng Chemical Co. China was purified further by recrystalline before use. Bisphenol A epoxy resin (model: CYD-128, 100 g resin containing 0.52 mole epoxy groups) was supplied by Yueyang Petrochemicals Company. 4,4′-diamino-diphenyl sulfone (DDS) curing agent was supplied by Shanghai Chemical Reagent Company.

Surface Modification on Nano-SiO$_2$

Nano-SiO$_2$ was dried under vacuum at 100 °C for 24 h to remove the physically adsorbing species before modification. The introduction of reactive groups onto the surface of nano-SiO$_2$ was obtained by the reaction of MPTMS with the hydroxyl groups of nano-SiO$_2$. A typical process was as follows: 10 g dried nano-SiO$_2$ was added to 350 mL ethyl alcohol, afterward, 20 mL distilled water and 11 mL (25%) ammonium hydroxide were added quickly to the above suspension. The nano-SiO$_2$ suspension was stirred for 90 min at room temperature in the presence of the ultrasonic, and then, MPTMS was added to the SiO$_2$ suspension and stirred for 1 h. The suspension was continually stirred for 24 h and then heated to reflux temperature to further react for 1 h. The suspension was evaporated to the appointed content by the rotary evaporator at the 40 °C then diluted to 0.1 g mL^{-1} by the addition of distilled water.

Synthesis of Waterborne Polyurethane (PU Prepolymer)

N220 (25.0 g, 12.5 mmol) was dehydrated under the vacuum at 100 °C and then added to the reactor together with TDI (5.6 g, 32.2 mmol). DMPA (1.0 g, 7.5 mmol) in DMF solvent was also added into the above reactor. Several drops of DBTDL were added in to catalyze the reaction. The mixture was stirred for 2 h at 70 °C under the atmosphere of dried and purified nitrogen, and the NCO content was detected on the basis of dibutylamine method in the reaction process.[20] The solvent butanone was added to the reactor to adjust the viscosity of the system. In succession, the mixture continued to react for 1 h after the addition of HPA (3.1 g, 23.8 mmol), and sequentially, the reaction went along for another 1 h at room temperature after the addition of the triethylamine. Finally, the waterborne polyurethane was prepared by agitation with high speed after the addition of the distilled water. The content of PU prepolymer was about 19.0 wt %.

Preparation of Nano-SiO$_2$/PMMA-PU Composite Particles

The modified nano-SiO$_2$ solution (50.0 mL), PU prepolymer latex (10.2 g), and MMA monomer(5.8 g) were added to the three necks flask. SE-10/OP-10 composite emulsifier and pH buffering agent NaHCO$_3$ were dissolved in 10 mL distilled H$_2$O and then added to the above mixture together with 7.0 g ethyl alcohol. The mixture was stirred for 30 min under the ultrasonic at room temperature. Initiator APS (0.15 g) was dissolved in 10 mL H$_2$O and dropped slowly into the reaction bottle with constant pressure funnel in the N$_2$ atmosphere, and then, the mixture reacted for 3 h at 80 °C. The emulsion was broken by the 2.5% aluminium potassium sulfate solution then extracted and washed repeatedly by distilled H$_2$O and ethyl alcohol. Finally, the power was dried at 80 °C under the vacuum condition, yield: 11.77 g.

Preparation of the Epoxy Resin Blend

The epoxy resin blend was prepared by referring to the equal equivalence of epoxy groups and active aminohydrogen in the DDS curing agent. A typical process was as follows: A certain amount of SiO$_2$-PMMA-PU composite particles was mixed with epoxy resin (30.0 g) in the dispersant and then stirred for 2 h under the ultrasonic. The curing agent DDS (10.0 g) was added to the above epoxy resin mixture and stirred for 10 min at 120 °C to be dissolved. The mixture was poured into a mold that had been heated at certain temperature beforehand, and then, the mold was degassed in a vacuum oven at 120 °C. The blends were heated and cured according to the 120 °C/2 h–160 °C/2 h–180 °C/2 h curing procedure.

Characterization

Fourier transform infrared spectra (FTIR) analysis was taken on an EQUINOX 55 instrument, and the FTIR spectrum was obtained with the KBr method. The morphology of the nano-SiO$_2$/PMMA composite particles was observed by using transmission electron microscopy (TEM, JEM-2010HR). The
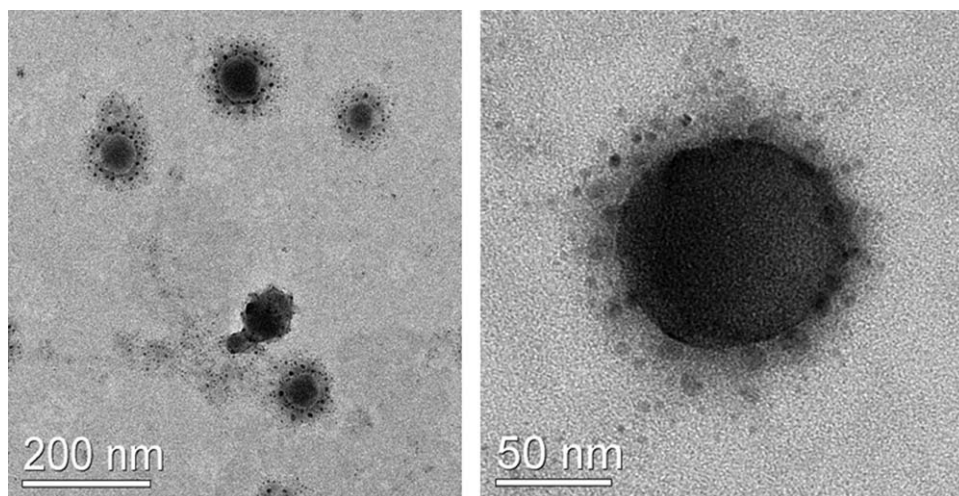
Figure 1. TEM morphology of nano-SiO$_2$/PMMA-PU composite particles.

emulsion was dispersed for 10 min with ultrasonic, then a drop of emulsion was put on a carbon-coated copper grid and dried in the vacumm chamber. X-ray photoelectron spectroscopy (XPS) data was collected by Thermo ESCALAB 250 photoelectron spectroscopy analyzer equipped with a Al $K\alpha$(1486.6 eV) source and was operated at 150 W and 1.0×10^{-7} Pa vacuum degree. Thermal gravimetric analysis (TGA) was studied with a TG-209F1 under a nitrogen atmosphere from 35 °C to 650 °C at a heating rate of 10 °C min^{-1}. No-notch impact strength of the cured epoxy resin samples was determined with a ZBC-1251-1 impact tester according to China National Standard GB/T 1843-2008. The sample size used for the test was $80 \times 10 \times 4$ mm^3. The average value of each sample which has at least three measurements was recorded, and the impact strength σ_1 is calculated by the equation: $\sigma_1 = 1000\ A/(bh)$, where A, b, and h is the impact energy, width and thickness of the sample, respectively.[21] Scanning electron microscope (SEM) was used to examine the fracture surface morphology of the samples after impact. The fracture surfaces were coated with thin layers of gold of about 100 A. All specimens were examined with a JSM-6700 F instrument at an activation voltage of 10.0 kV.

RESULTS AND DISCUSSION

Structure and Morphology of Nano-SiO$_2$/PMMA-PU Composite Particles

The morphology and size of the composite particles are firstly characterized by transmission electron microscopy (TEM) as shown in Figure 1, the morphology of which is spheral and the diameter is 50–100 nm. The particles have smooth surface without any attached or adsorbed nano-SiO$_2$, and no free nano-SiO$_2$ is found in the composite particles. In the composite particles, the 30–60 nm dark SiO$_2$ locates in the centre of particles, the surface of which is encapsulated by 20-30 nm light PMMA and PU. For the shell polymer, the dark region is PU domains with about 10 nm diameter,[22,23] the light region is PMMA domains, and the reason is that the electronic cloud density around the PU chains is higher than that around PMMA chains. The PU microdomains well distributed in PMMA polymer, indicating that the PU has excellent compatibility with

PMMA. From the above result, the nano-SiO$_2$ has been effectively encapsulated by PMMA-PU, and thus, the composite particles form the obvious core-shell structure, which should contributed to the very good compatibility between PMMA and PU together with the emulsion polymerization on the surface of the nano-SiO$_2$. The possible formation process is shown in Scheme 1. The hydrophobic MMA monomer will form free micelles together with the PU prepolymer influenced by the composite emulsifier SE-10/OP-10. The core nano-SiO$_2$ particles with large ratio surface can absorb the free micelles and MMA monomer;[24,25] moreover, the formed micelles including the nano-SiO$_2$ will be stabilized by absorbing the composite emulsifier SE-10/OP-10. The core-shell composite particles are successfully prepared when the APS initiator radicals enter into these micelles from aqueous phase to initiate MMA and PU prepolymer polymerization. The PMMA and PU polymer as the shell layer encapsulate on the surface of nano-SiO$_2$.

FTIR Spectra of Nano-SiO$_2$/PMMA-PU Composite Particles

The successful synthesis of nano-SiO$_2$/PMMA-PU composite particles was also confirmed by Fourier transform infrared spectroscopy (FTIR) as shown in Figure 2. The FTIR spectrum of the modified nano-SiO$_2$ (Figure 2a) presents the absorption peak at 2958 cm^{-1}(v-CH$_3$) and 1710 cm^{-1}(v-C=O), which indicates clearly that the coupling agent MPTMS is bonded to the surface of SiO$_2$. For the spectrum of nano-SiO$_2$/PMMA-PU composite particles (Figure 2b), the peaks at 3378–3448 cm^{-1} should belong to the NH group of PU and —OH group of original nano-SiO$_2$, and the peaks at 2986 cm^{-1} and 2954 cm^{-1} should attribute to the C—H bond stretching absorption of PMMA and PU. The spectrum also exhibits the typical absorption peak of PMMA at 1738 cm^{-1}(C=O bonded stretching libration), indicating clearly that PMMA is bonded to the surface of SiO$_2$. The absorption peak at 1000–1260 cm^{-1} should attribute to Si—O bond stretching libration of nano-SiO$_2$ and C—O (ether bond) stretching vibrations of PMMA.[26,27] Overall, the spectrum presents the composite structure of SiO$_2$, PMMA, and PU; moreover, the characteristic peaks of 1100 cm^{-1} and 476 cm^{-1} do not change, indicating that the formation of SiO$_2$/
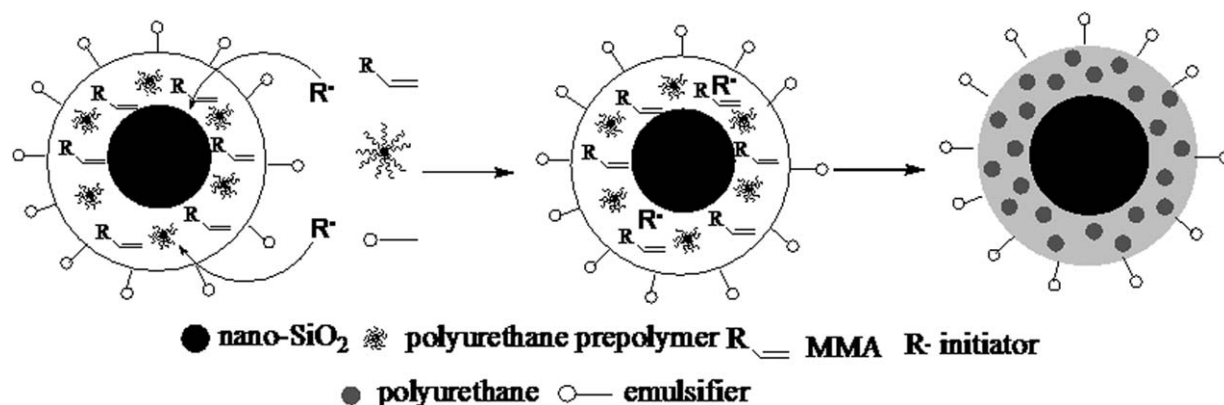
Scheme 1. The possible formation process of nano-SiO$_2$/PMMA-PU composite particles

PMMA-PU composite particles does not affect the whole ingredients and crystal structure of nano-SiO$_2$.

Surface Analysis of Nano-SiO$_2$/PMMA-PU Composite Particles

Since the surface property of materials is associated compactly with their surface chemical ingredients, it is very important to investigate the surface chemical ingredients.[16] X-ray photoelectron spectroscopy (XPS), as another important spectroscopic technique, can directly detect the surface structure (2–10 nm) of materials and provide the surface information, such as elemental composition, chemical status, empirical formula, electronic state or binding modes of surface ligands, and depth analysis or atomic composition with depth,[28] so it can investigate the encapsulation effect from the change of the element content before and after encapsulation. When the nano-SiO$_2$ is effectively encapsulated by PMMA and PU, the Si content should decrease rapidly even be close to zero, but the C content should increase rapidly. The full-scanning XPS spectrum of the nano-SiO$_2$/PMMA-PU composite particles is exhibited in Figure 3, which presents the strong signals of C1S and O1S as well as the weak signals of N1S, Si2S, and Si2P. The content of C, O, N, and Si element is, respectively, 65.29%, 31.36%, 1.27%, and 2.08%, and the 2.08% little Si content should attribute to the unencapsulated Si besides the hydrolysis and condensation of

MPTMS.[14] The presence of N1S signal confirms further PU existence in composite particles. All these results indicate that the surface of nano-SiO$_2$ has been encapsulated successfully by PMMA and PU.

Thermal Gravimetric Analysis (TGA) of Nano-SiO$_2$/PMMA-PU Composite Particles

The thermal stability of the obtained composite particles was further investigated by thermal gravimetric analysis (TGA) as shown in Figure 4. When the temperature is less than 130 °C, the weight loss is about 2.7%, which should contribute to the adsorbing H$_2$O on the particles surface. The TGA curves have two decomposition stages at 250 °C and 350 °C which should be, respectively, aroused by the thermal decomposition of PU and PMMA, because the extra N atom in the PU may decrease its thermal stability compared with PMMA. In order to further investigate the encapsulation effect of the nano-SiO$_2$, the composite particles are extracted by toluene for 24 h to remove the physically adsorbing PMMA and PU on the surface of nano-SiO$_2$. The TGA curve of the extracted particles is also described in the Figure 4. Compared with the original composite particles, PU fraction in the extracted particles does not obviously change besides that a little of PMMA is extracted, which indicates that most PMMA and PU grafted to the surface of the nano-SiO$_2$ mainly depends on the covalent bond type. The ratio of PMMA-PU to original SiO$_2$ (f_p), the grafting ratio to original
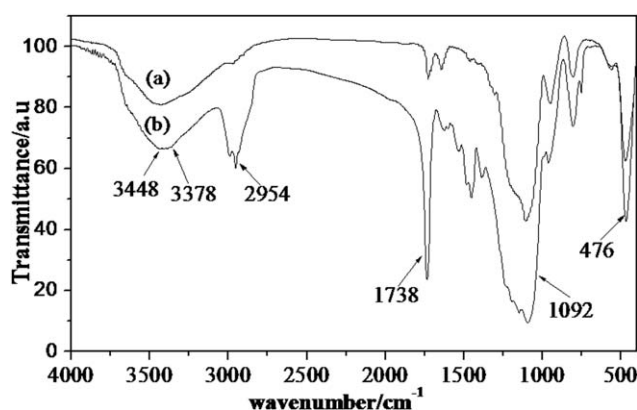

Figure 2. FTIR spectra of the modified nano-SiO$_2$ by MPTMS and nano-SiO$_2$/PMMA-PU composite particles. (a) the modified nano-SiO$_2$ by MPTMS; (b) the nano-SiO$_2$/PMMA-PU composite particles.
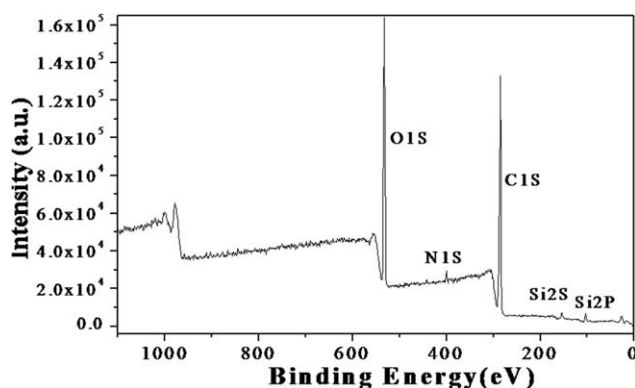

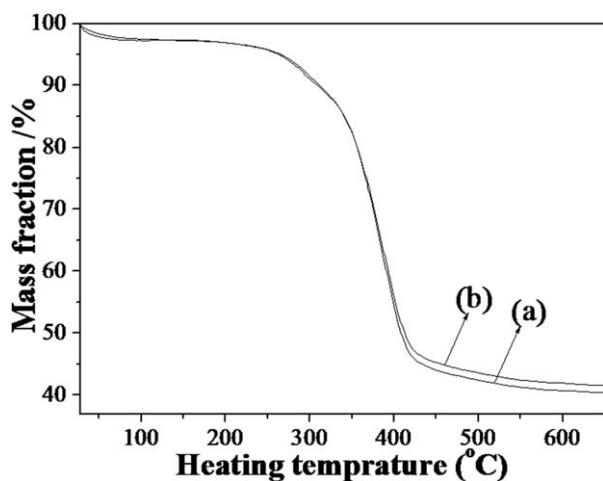**Figure 3.** XPS full-scanning spectrum of nano-SiO$_2$/PMMA-PU composite particles.

Figure 4. TGA thermograms of the original and extracted nano-SiO$_2$/PMMA-PU composite particles. (a) the original nano-SiO$_2$/PMMA-PU composite particles; (b) the extracted nano-SiO$_2$/PMMA-PU composite particles.

SiO$_2$ (f_r) and efficiency grafting of PMMA-PU (f_e), each is calculated as follows:

$$f_p = \frac{\text{PMMA-PU formed (g)}}{\text{SiO}_2 \text{ added (g)}} \times 100\% \qquad (1)$$

$$f_r = \frac{\text{PMMA-PU unremoved by extraction (g)}}{\text{SiO}_2 \text{ added (g)}} \times 100\% \qquad (2)$$

$$f_e = \frac{\text{PMMA-PU unremoved by extraction (g)}}{\text{PMMA-PU formed (g)}} \times 100\% \qquad (3)$$

On the basis of the above TGA curves, the f_p value is about 116.7% from the unextracted sample (Figure 4a), the f_r value is about 104.4% from the extracted sample (Figure 4b) and the f_e value is about 89.5% from the relation of f_p and f_r.

The Application of Nano-SiO$_2$/PMMA-PU Composite Particles in Epoxy Resin

The effect of the different nano-SiO$_2$/PMMA-PU content on the impact strength of epoxy resin is described in Figure 5. The impact strength increases firstly and then decreases with a maximum value of 46.64 kJ m^{-2} at 5 wt % of the nano-SiO$_2$/PMMA-PU (Figure 5a). The impact strength of the modified epoxy resin is about 2–3 times of the value observed for the unmodified epoxy resin, which indicates that the addition of nano-SiO$_2$/PMMA-PU into epoxy resin can remarkably improve its toughness. Ma *et al.* also reported the similar conclusion that silica nanoparticles could increased the energy release rate (G_{1C}) of epoxy resin with 81% improvement compared with the neat epoxy cured at 130 °C.[19] The reason that the impact strength increases with the content of nano-SiO$_2$/PMMA-PU in the epoxy resin matrix increasing is that the inorganic nano-SiO$_2$/PMMA-PU can restrict the crack developing further when the epoxy resin is destroyed. The surface of the nano-SiO$_2$/PMMA-PU has the active group NH which can react with the epoxy group, enhancing the binding power of the interface of nanoparticles and epoxy resin matrix. When epoxy resin is affected by the outside force, on one hand, the nanocomposite particles play the role of stress concentration and induce the abundance of crazes, so it can detract and consume a great deal of impact energy; on the other hand, the shell layer can control the crazes expanding and make the crazes terminate but not form the devastating crack. When the content of the nano-SiO$_2$/PMMA-PU is beyond 5 wt %, the impact strength goes down, and the reason should be that the content increasing further will arouse the nanoparticles agglomerating.

Scanning electron microscopy (SEM) of the fracture surfaces of the neat and modified epoxy resin blend are also shown in Figure 5. The neat epoxy resin appears as a smooth, glassy, and linearly fractured surface (Figure 5b), which indicates that the resistance is very little in the fracture process. It is the typical brittle fracture.[29] By contrast, SiO$_2$/PMMA-PU modification changes the fracture surface from the smooth to the rugged (Figure 5c), which suggests that the fracture surface undergoes much resistance in the fracture process and plastic deformation occurs, preventing the propagation of cracks and inducing higher fracture toughness.[30,31] Energy is absorbed during plastic deformation in the modified blend, and it is the obvious toughness fracture.

CONCLUSIONS

In summary, we have developed a new method of hybrid nano-SiO$_2$/PMMA-PU particles to modify epoxy resin. The composite particles were firstly prepared basing on the emulsion
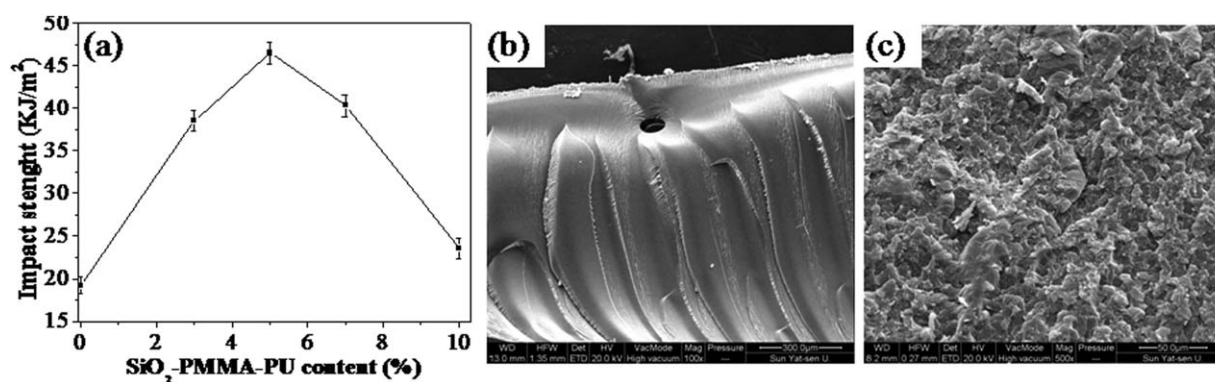

Figure 5. The effect of nano-SiO$_2$/PMMA-PU content on the impact strength of epoxy resin and the SEM micrographs of the fracture surfaces. (a) impact strength of epoxy resin; (b) the SEM of neat epoxy resin; (c) the SEM of modified epoxy resin with 5% nano-SiO$_2$/PMMA-PU

polymerization of MMA and PU prepolymer on the surface of nano-SiO_2. The composite particles have the 50–100 nm diameter and obvious core-shell structure with dark core SiO_2 (30–60 nm) and light shell polymer (20–30 nm). The content of C, O, and Si on the surface of the composite particles is, respectively, 65.29%, 31.36%, and 2.08% with the 1.27% N content. The ratio of polymer to original nano-SiO_2 (f_p), the grafting ratio of polymer to original nano-SiO_2 (f_r) and efficiency grafting ratio of polymer (f_e) were, respectively, about 116.7%, 104.4%, and 89.5%. With the 5 wt % nano-SiO_2/PMMA-PU in the epoxy resin matrix, the impact strength increases to 46.64 kJ m^{-2} from 19.12 kJ m^{-2} of the neat system. Considering their excellent performances, thus obtained nano-SiO_2/PMMA-PU particles are expected to have a high potential for fabrication of hybrid nanoparticles and their application in polymer composite materials.

ACKNOWLEDGMENTS

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