The Surface Modification of Nanosilica, Preparation of Nanosilica/Acrylic Core-Shell Composite Latex, and Its Application in Toughening PVC Matrix

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ABSTRACT: The properties and morphology of nanosilica modified with silane coupling agent, methacryloxypropyltrimethoxysilane (MPS), were characterized by fourier transform infrared, zeta potentials, thermogravimetric analysis, and transmission electron microscopy. The results showed that the grafting ratio of MPS on the surface of nanosilica increased with the MPS content. MPS-silica/PBA/PMMA core-shell latexes (MPS-Si/ACR) were prepared by seeded emulsion polymerization. Then they were used to mix with PVC resin. The outer layer (PMMA) enhanced the dispersibility of MPS-Si/ACR in the PVC matrix by increasing the interfacial interaction of these composite particles with PVC. The notched impact strengths of the blends were influenced by the weight ratio of MPS to silica, the concentration of emulsifier (SDS), and the MPS-Si/ACR content. The relationships between the mechanical properties and the core-shell composite structures were elaborated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2671–2680, 2008

Key words: silicas; emulsion polymerization; poly(vinyl chloride); blends; structure-property relations

INTRODUCTION

Organic–inorganic composite particles with well-defined morphology and structure controlled at the nano scale represent a very interesting class of materials both for their use as fillers or as reinforcement of polymeric matrices because of their potential use in a wide range of technologically advanced and more conventional application fields.[1] Various nanofillers, including montmorillonite,[2] silica,[3] calcium carbonate[4], and aluminum oxide,[5] have been reported to enhance mechanical and thermal properties of polymers, such as toughness, stiffness, and heat resistance. However, it is difficult for nanoinorganic particles to disperse in polymer matrix at the nano scale, because the surface energy of the tiny particles is very high and these particles tend to agglomerate during mixing.[6] To achieve a good dispersion of inorganic compound and to increase interface adhesion between the polymer and fillers, physical or chemical approaches have been used to modify the surface of nanoparticles.[7] Generally, the approaches which have been tried to solve the problems are the vapor deposition technique,[8] grafting-from technique,[9] grafting-into technique,[10,11] mechanical and chemical treatment technique,[12] plasma treatment technique,[13] and so on.

Nanosilica is one of the most common nanofillers used in the preparation of nanocomposites. The grafting of organosilane coupling agents on nanosilica surface had been the subject of many investigations in the past.[3] The silane coupling agent can form chemical bond and strong interactions between nanoparticle and matrix. Effectiveness of reinforcement for the polymer depends on the nature of the coupling agent covering the particles surface and the dispersion state of inorganic particles in the polymer matrix.[14,15] Effective bonding between the filler and matrix component typically by modifying fillers with silane coupling agent improves the mechanical properties of nanosilica polymer composites.[16] This modification of the silica and alumina nanoparticles was accomplished by methacryloxypropyltri-methoxysilane, vinyltri-methoxysilane, and glycidyloxypropyltrimethoxysilane. Modified composite materials

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exhibit markedly improved properties as compared with the neat acrylate polymer.[17] Selection of reaction conditions makes possible the preparation of composite particles that contain one core of silica and obtains sufficient dispersion.[18]

Poly(vinyl chloride) (PVC), a commodity plastic, has been widely used in industrial fields due to its good properties, such as nonflammability, low-cost, and formulating versatility. However, its low toughness and heat-distortion temperature limit its application. In the past, a variety of PVC blends with other resins (for example, PMMA, MBS, CPE, NBR) were developed to broaden PVC application.[19–22] P(MMA-St) was reported to be compatible with PVC and had a positive toughening effect on PVC.[23]

In recent years, nanocomposites based on PVC have attracted great attention. PVC/nano-$CaCO_3$,[4] PVC/nanosilica,[24] and PVC/nano-Sb_2O_3[25] nanocomposites have been studied. Silica exhibits specific physicochemical and surface properties after the modification. The surface becomes more hydrophobic, exhibiting augmented affinity to organic polymer.[26,27] In this article, we characterize the changes on the silica surface properties modified with a coupling reagent, methacryloxypropyltrimethoxy silane (MPS) by Fourier Transform Infrared (FTIR), X-ray Photoelectron Spectrometer (XPS), Thermogravimetric Analysis (TGA), zeta potential, and Transmission Electron Microscopy (TEM). MPS-silica/PBA/PMMA (MPS-Si/ACR) composite latexes are synthesized successfully through seeded emulsion polymerization. The mechanical properties of MPS-Si/ACR and PVC blends are also investigated.

EXPERIMENTAL

Materials

Fumed silica (A200) particle diameter, 15 ± 5 nm, was supplied from Shenyang Nanji Chemical Industry, China. Prior to use, the particles were dried in an oven at 110°C under vacuum for 4 h to get rid of the physically absorbed and weakly chemisorbed species. The coupling agent, methacryloxypropyltrimethoxy silane (MPS), supplied by Nanjing Shuguang Chemical Reagent, China, toluene and ethanol (AP), purchased from Tianjin Chemical Reagent, China, dilute hydrochloric acid (AP), purchased from Tianjin No. 3 Chemical Reagent Factory, were used as received. *n*-butyl acrylate (BA) was washed three times with 2% sodium hydroxide solution and deionized water, dried over $CaCl_2$ overnight, and then distilled. Methyl methacrylate (MMA), CP, from Tianjin Chemical Reagent Factory, was distilled under the reduced pressure. 1,4-butanediol diacrylate (BDDA) and Allyl methacrylate (ALMA), CP, were purchased from Tianjin Tianjiao Chemical, China. Sodium dodecylsulfate (SDS), AR, was from Tianjin Kermel Chemical Reagents Development Centre, China, and Potassium persulfate ($K_2S_2O_8$), AR, from Tianjin University Chemical Reagent Factory, China. They were used without purification. PVC resins (SKL-1000) was purchased from Tianjin Dagu Chemical. Deionized water was used for all polymerization and modification process.

Modification of nanosilica particles

Grafting reaction was carried out in toluene (120 mL) at the reflux temperature under N_2 atmosphere. Dried nanosilica (4 g) was suspended in toluene under mechanical stirring and ultrasonic dispersing. The weighed MPS was dissolved in ethanol (10 mL) and adjusted pH values, and then mixed with nanosilica in flask. The adduct was heated and reacted for 1 h at the reflux temperature, cooled to room temperature, and separated by centrifugation. After drying at 90°C under vacuum, the mixture was extracted using Soxhlet extractor for 12 h using toluene. The product was finally dried at 90°C under vacuum condition for 24 h.

Preparation of MPS-silica/PBA/PMMA core-shell (MPS-Si/ACR) composite latexes

Nanosilica particles modified with MPS (MPS-Si) were emulsified in water containing the emulsifier, SDS, by the mechanical stirring and ultrasonic dispersing, and adjusting the pH value to 8–10 with sodium hydroxide solution. The amounts of the components were listed in Table I. After the seeded pre-emulsion was introduced into the reaction vessel, and heated to 73°C, it was deoxygenated by bubbling with high pure nitrogen for 20 min. Then a certain amount of initiator (KPS) solution, monomer (BA), crossing-link agent (BDDA), and grafting agent (ALMA) were dropped into the seeded latex at a rate of about 10 droplets per minute. After emulsion polymerization was carried out for 40 min, a small

TABLE I
Recipe of Synthetic MPS-Si/ACR Composite Latex

	Component	Mass/g
Seed stage	MPS-silica	6
	SDS	0.5
	H_2O	150
Growth-stage		
Core layer	BA	18
	BDDA	0.18
	ALMA	0.18
	KPS/H_2O	0.72/10
	SDS	0.36/15
Shell layer	MMA	12
	KPS/H_2O	0.48/10
	SDS	0.24/15

amount additional emulsifier (SDS) was added each hour. When the monomers were dropped completely, the core growth-stage of polymerization was maintained for 1 h at 73°C. Introducing the residual initiator, the latex started to drop MMA monomer at a rate of about six droplets per minute. The system was maintained at 73°C for 1 h after the monomer was dropped completely. The composite latex was refrigerated to coagulate and demulsify, and then the precipitated materials were filtered, washed, and dried under vacuum at 50°C to get MPS-Si/PBA/PMMA (MPS-Si/ACR) particles.

Preparation of blending samples with MPS-Si/ACR particles and PVC resin

The synthesized MPS-Si/ACR particles were mixed with PVC resin and other determined quantity additives. The processing recipe was 100 parts of PVC resin, 3 parts of organotin, 0.6 part of calcium stearate, 0.6 part of stearyl alcohol, and different parts of MPS-Si/ACR. All components were first premixed in a high-speed mixer at room temperature and then processed on a laboratory two-roll mill between 170 and 175°C for 7 min. Two or four millimeter-thick plates were pressed at the temperature of 178–182°C. The plates were cooled under a cooling press.

Characterization

FTIR measurement

The extracted samples of the modified nanosilica and paraffin oil were pulverized and analyzed by infrared spectrometric analyzer (Bruker Vector-22).

XPS measurement

XPS images of the bare nanosilica and the modified nanosilica were collected with a ESCALAB 250 apparatus (Thermo Electron) to illuminate the interaction between the particles and the grafted silane coupling agent.

Zeta potential, the particle diameter and its distribution measurement

The modified nanosilica was suspended in water to prepare aqueous suspension of 1 wt % under mechanical stirring and ultrasonic dispersing. The change of zeta potential of the modified nanosilica was determined by Malvern Instrument, Zetasizer HS3000. The particle diameter distributions of composite latexes synthesized by seeded emulsion polymerization were also obtained by photon correlation spectroscopy (PCS) from the same instrument.

TGA measurement

The modified nanosilica particles were Soxhlet extracted with toluene. The grafting ratio of MPS on the surface of nanosilica was measured using a TGA (Dupont STD-2960) at a rate of 10°C/min under nitrogen atmosphere.

The grafting ratio (R_g) was calculated according to the following equation:

$$R_g = \left(\frac{W_1'}{W_1} - \frac{W_0'}{W_0} \right) \times 100\%$$

where, W_1 is the starting weight of the modified nanosilica particles, W_1' residual weight of the modified nanosilica particles at 750°C, W_0 the starting weight of unmodified nanosilica particles, W_1' the residual weight of unmodified nanosilica particles at 750°C.

TEM observation

Modified and unmodified nanosilica particles were suspended in ethanol by mechanical stirring and ultrasonic dispersing, while the MPS-Si/ACR composite latex was suspended in water. A drop of diluted dispersion was put on a carbon film supported by a copper and placed in the HITACHI H-800 TEM. The MPS-Si/ACR particles dispersed in PVC matrix were determined by TEM. The samples were directly observed without dyeing.

Impact strengths of MPS-Si/ACR composite particles and PVC blends

The tensile properties were measured on an Instron (model 1122) tensile machine (Buckinghamshire, UK) according to ASTM D 638 with a crosshead speed of 5 mm/min at room temperature. The Charpy notched impact tests on the specimens were carried out with a pendulum-type impact tester (CXJ-40, Chengde Testing Instruments, Chengde, China) at room temperature. At least five runs were made so we could report the average.

Scanning electron microscopy measurement

A Philips XL30 Scanning Electron Microscope (SEM) was employed to study and record the fractured surfaces of all the mixing samples. The fractured specimen surfaces were coated with a thin layer of gold. The coating was carried out by placing the specimen in a high vacuum evaporator and vaporizing the metal held in a heated tungsten basket.

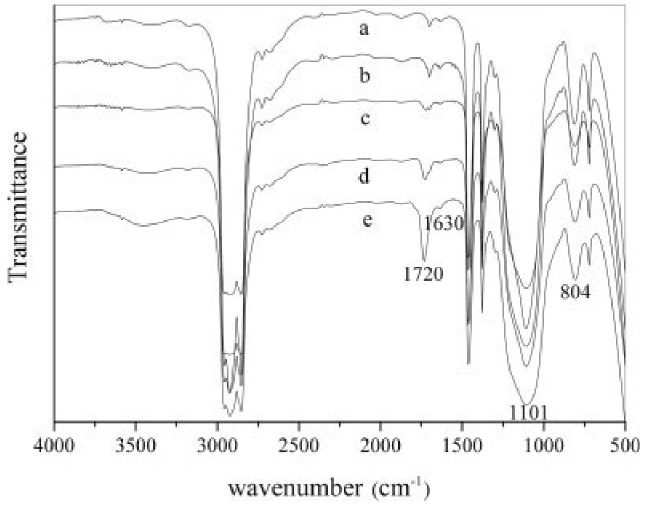


Figure 1 FTIR spectra of nanosilica modified with the different weight ratios of MPS to nanosilica (a) 3%, (b) 5%, (c) 10%, (d) 15%, (e) 25%.

TABLE II
Zeta Potential and Grafting Ratio on the Surface of Silica Modified with MPS at Different Modification Conditions

Reaction condition	Zeta potential (mV)	Grafting ratio (wt %)
pH value		
2	−11.072	6.58
3	−9.872	6.62
4	−8.179	6.92
6	−8.400	4.69
6.5	−8.841	4.15
Reaction time (min)		
30	−7.902	0.81
50	−7.622	1.20
80	−7.148	2.97
90	−7.089	6.92
100	−7.268	5.84
110	−7.981	5.68
MPS/silica (wt %)		
3	−11.081	4.10
5	−8.971	5.58
10	−7.813	6.92
15	−7.297	8.80
25	−6.555	13.07

RESULTS AND DISCUSSION

Modification of silica with MPS

FTIR and XPS spectra of the modified nanosilica

Figure 1 illustrated the FTIR absorption spectra of the modified nanosilicas with different weight ratios of MPS to silica. The characteristic bands at 1101 and 804 cm^{-1} could be associated with Si—O symmetric stretching and asymmetrical stretching absorption bands of nanosilica, respectively. The characteristic band at 1720 cm^{-1} was relative to C=O symmetric stretching absorption bands of MPS.[28,29] As the samples were extracted by Soxhlet extraction with toluene, the physical absorbed MPS had been removed. In the grafting process, silane coupling agents were first hydrolyzed to form an organosilanetriol, and then organosilanetriol, which reacted with —OH on the surface of silica to form Si—O—Si bonds. The FTIR absorption spectra of the extracted MPS/nanosilica samples could be tentatively ascribed to chemical bonding, i.e., the amount of the grafted MPS on the surface of nanosilica increased with the increase of the amount of MPS in the treatment systems. The results from TGA were listed in Table II.

The extracted MPS/nanosilica was also characterized by XPS.[30] From XPS spectra in Figure 2, it could be seen that the binding energies of Si 2s and Si 2p in the modified version were 159.1 and 108.4eV, while they were 160 and 109eV in the original version. There were 0.9 and 0.6eV shifts to the low binding energies after the silica particles were modified. This shift was caused by the change of the chemical environments where the atoms existed. Electrons around C—O transferred to O—Si due to the weaker electronegativity of Si than that of C. Hence, the electronic density around Si atoms increased, causing the binding energy to become lower. Both FTIR and XPS spectra told us that MPS molecules had been effectively grafted on the surface of nanosilica particles.

TGA curves of the modified nanosilica

Figure 3 shows the curves of TGA for the modified nanosilica with different pH values. The decomposition ratio of organic compounds increased and then decreased with the pH value. As the modified nanosilica particles were extracted with toluene for 12 h, the MPS absorbed physically was removed completely. So it could be thought that the decomposi-

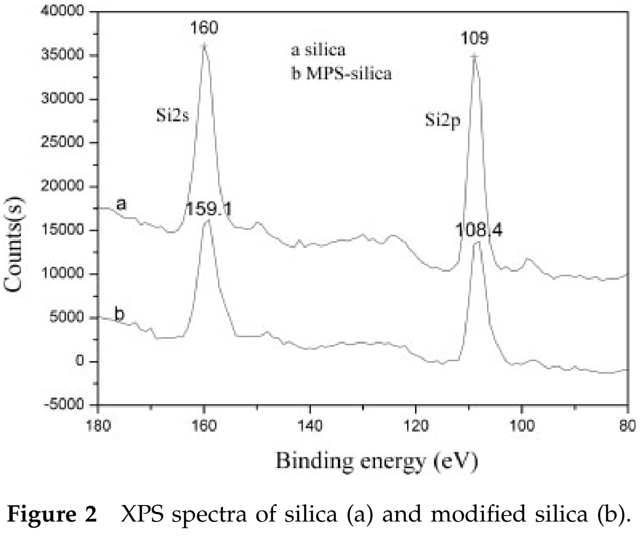


Figure 2 XPS spectra of silica (a) and modified silica (b).

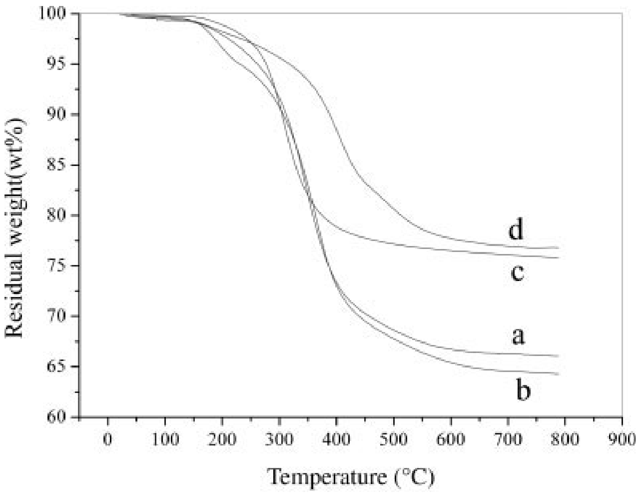


Figure 3 The TGA curves of residual weight percent of modified nanosilica (a) pH = 2, (b) pH = 4, (c) pH = 6, (d) pH = 6.5.

tion ratio of organic compounds was equal to grafting ratio.[31] The more the weight loss, the higher the grafting ratio. The results are listed in Table II also.

Effect of the modified nanosilica on zeta potential

Modified nanosilica particles were suspended in water and would generate weak silicic acid due to ionization. Some of them adhered to the surface of nanosilica to form a colloid core with negative electricity, zeta potentials generated because an electric double layer was formed on the nanosilica surface.[32,33]

In general, the zeta potential was an important factor controlling the dispersion stability of silica suspensions, which resulted in the existence of an energy barrier preventing the proximity of particles.[34–36] A minimum of surface charge was needed for the dispersion of powders in aqueous suspension. After the silica particles were modified with MPS, absolute value of the zeta potentials would change to some degree in the process. In this part, we studied the effect of zeta potentials on the surface of nanosilica treated with MPS from some factors, such as pH value, the weight ratio of MPS to nanosilica and reaction time.

Table II summarized the results of the zeta potential and grafting ratio. It was found that absolute values of the zeta potentials first reduced, and then increased with pH value. The trend was the same as that of the reaction time. There were three kinds of reaction, hydrolysis of silane coupling agent, condensation of silantriols, and condensation between silantriols and —OH of nanosilica surface. A greater amount of MPS could be grafted if the MPS was first hydrolyzed and partly condensed, and then reacted with nanosilica.[16] At pH below 4 or 5, silica was stable (against aggregation and sedimentation) even when up to about 1.0*M* of any noncovalent salt was added. The deceased absolute value of the zeta potential was profitable, and the capacity of absorbing water reduced, i.e., hydrophilicity on the surface of silica deceased and exhibited augmented affinity to organic compounds, such as BA monomer. It was useful to prepare core-shell latex particles by emulsion polymerization. But with the extension of reaction time, the oligomeric siloxanol increased obviously by self-condensing between silantriols, and space steric hindrance of formed oligomers was larger. Silantriols of hydrolysis of silane coupling agent increased with the content of MPS. The tight chemical bond also was raised by condensation between silantriols and —OH of nanosilica surface, where multilayer coverage was formed on the surface of silica. The hydrophobization of silica gradually increased, reversely, the hydrophilication gradually weakened.

Morphology of modified and unmodified nanosilicas

The morphologies of unmodified and modified nanosilica were characterized by Transmission Electron Microscopic (TEM), as shown in Figure 4. We could observe apparently that the unmodified nanosilica exhibited a large number of agglomerates from Figure 4(a), while the loose structure and uniform dispersion of MPS modified nanosilica were observed from Figure 4(b). After nanosilicas were modified with MPS, the hydrophobization gradually raised and its hydrophilicity weakened on the surface of nanosilica, and their surface energy was also reduced so as to weaken the trend of agglomeration.

Preparation of MPS-silica/PBA/PMMA (MPS-Si/ACR) composite particles

The particle diameter and its distribution of MPS-Si/ACR core-shell composite latexes at different synthetic stages

The particle size and distribution of composite latexes (MPS-Si/ACR) in different synthetic stages were shown in Figure 5. When the first-stage emulsion polymerization was completed, the average particle size of MPS-silica/PBA (core layer) was about 35 nm, obviously larger than the particle mean size of nanosilicas (15 nm). It indicated that the PBA had encapsulated on the surface of MPS-silica. The particle size of MPS-Si/ACR latex particle increased to 47 nm when second-stage emulsion polymerization was over. The polydispersities of their distributions of two synthetic stages were both less than 0.2. This showed that monomer of BA and surfactants could be adsorbed onto the surface of MPS-silica, and sur-

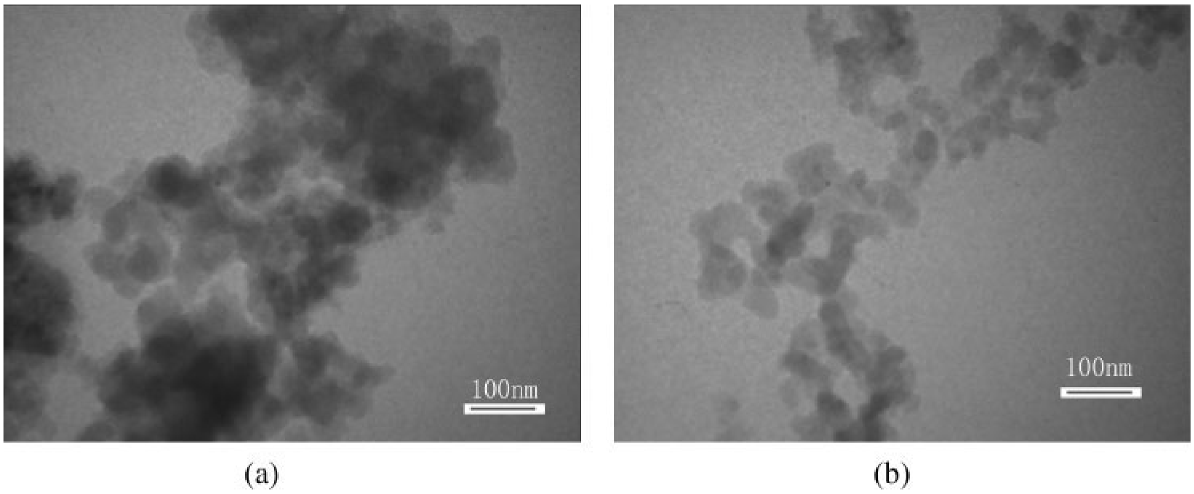


Figure 4 TEM images of silicas dispersed in ethanol (a) unmodified nanosilica, (b) modified nanosilica by MPS.

factants acted as micelles to ensure the polymerization took place around the MPS-silica. The silica particles were modified with MPS to introduce vinyl groups onto the particle surfaces which were facilitated to prepare silica/polyacrylate core-shell particles.[37,38] The morphology of MPS-Si/ACR composite latex was observed by TEM, as shown in Figure 6. It could be seen that the particles consisted of a dark core which was silicon dioxide and a brighter shell which was the polymer. The image indicated that the particles of the silica modified with the silane coupling agent (MPS) were mainly separated and enwrapped by the polymer.

Effect of the concentration of SDS on emulsion particle diameter

Figure 7 showed that the latex diameter decreased with the increase of the concentration of emulsifier (SDS). When the concentration of emulsifier was larger than CMC, the secondary latex particles generated easily with the increase of emulsifier, and the latex particle diameter decreased. So the concentration of SDS was critical to the latex diameter.[39] In this experiment, the concentration of SDS was larger than CMC. In the emulsion polymerization process, stability of emulsion would decrease because the density of the charge on the latex particle surfaces decreased gradually when the latex particles grew larger. A small amount of additional emulsifier could guarantee stability of emulsion and reduced to cause the secondary nucleation.

Blending of MPS-Si/ACR compound particles with PVC resin

TEM microphotographs of dispersion of MPS-silica/ACR particles in PVC matrix

Dispersion of MPS-Si/ACR composite particles in the PVC matrix had significant effects on the

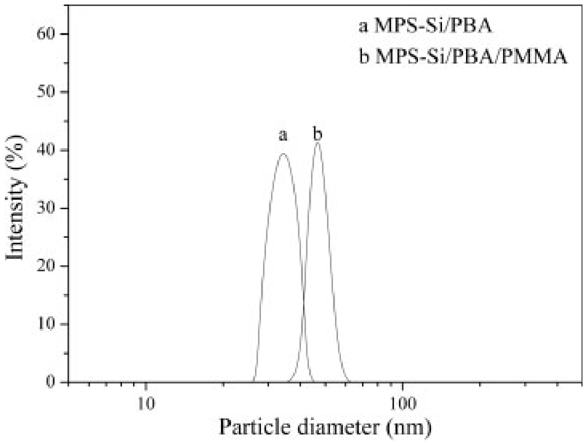


Figure 5 Particle diameter distributions of MPS-silica/BA (a) and MPS-Si/BA/MMA (b) latexes.

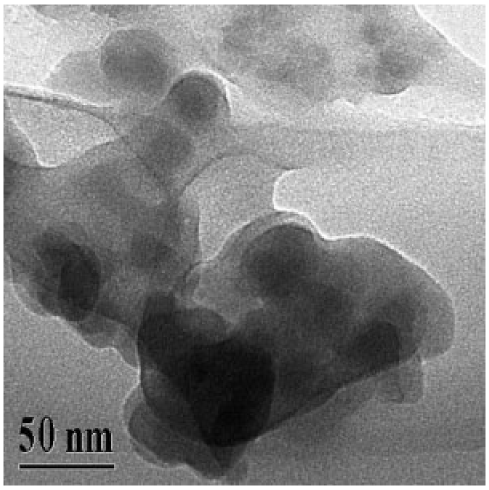


Figure 6 TEM image of MPS-Si/ACR composite latex.

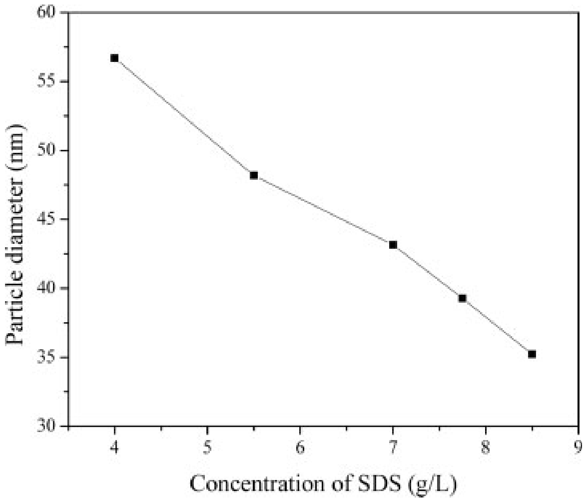


Figure 7 The curve of the particle diameter versus the concentration of SDS.

mechanical properties of the blends, especially, when the filler size of nanosilica decreased to nanometer scale. In Figure 8, MPS-Si/ACR particles are uniformly dispersed in the PVC matrix with an average size of 40–50 nm.

Mechanical properties of MPS-Si/ACR/PVC blends

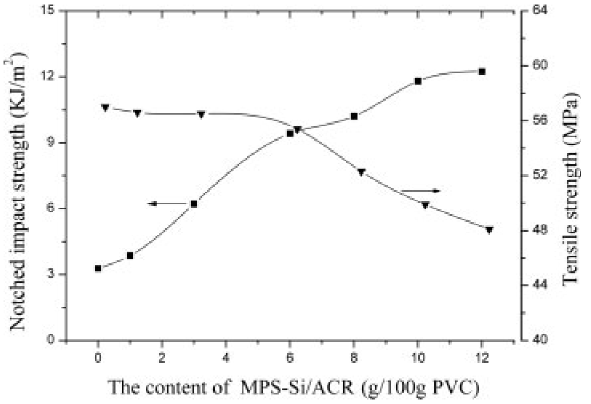


Figure 9 The curve of the mechanical properties of the blends of the different MPS-Si/ACR contents with PVC resin.

Figure 9 plotted the variation of notched impact strength of MPS-Si/ACR/PVC composite with the different contents of MPS-Si/ACR. We could see from Figure 9 that the notched impact strength of the blends increased with the content of MPS-Si/ACR, while the tensile strength of the blends started to decrease after the MPS-Si/ACR content was over 6 g/100 g PVC. The results demonstrated the role of grafting polymers (ACR), i.e., interconnecting the nanosilica particles through chemical bonding and correlating the grafted nanosilica particles with the PVC matrix by chain entanglement which guaranteed effective interfacial bonding. PMMA (the shell layer), having a solubility parameter very close to that of PVC (the matrix), is expected to have a very good compatibility with PVC.[40] The phenomenon of stress concentration caused by the addition of MPS-Si/ACR particles in the PVC matrix could be changed via the interaction of composite particles and PVC molecule chains, as well as the effect of interfacial energy transmission. This led to the improvement of the impact toughness of the blends. Meanwhile, a low modulus layer (PBA) around the modified silicas was able to support a main part of the deformation, limiting the decrease in tensile strength due to the adding of MPS-Si/ACR particles. Therefore, we chose the MPS-Si/ACR content of 6 g/100 g PVC in the following discussion.

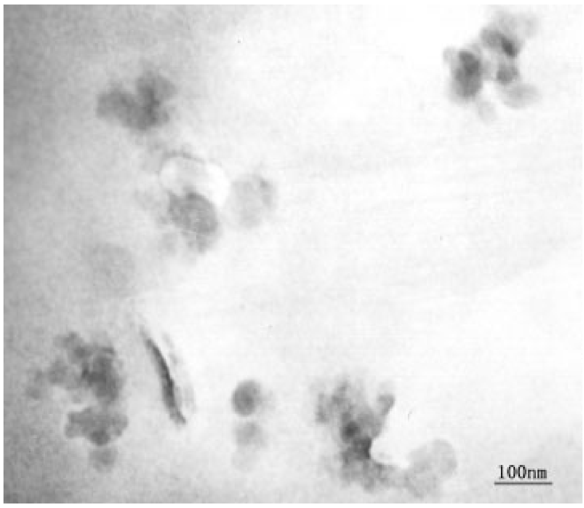


Figure 8 TEM image of MPS-Si/ACR/PVC blend (the weight ratio of MPS-Si/ACR to PVC: 6/100).

The notched impact strength of the MPS-Si/ACR/PVC blends increased with the concentration of

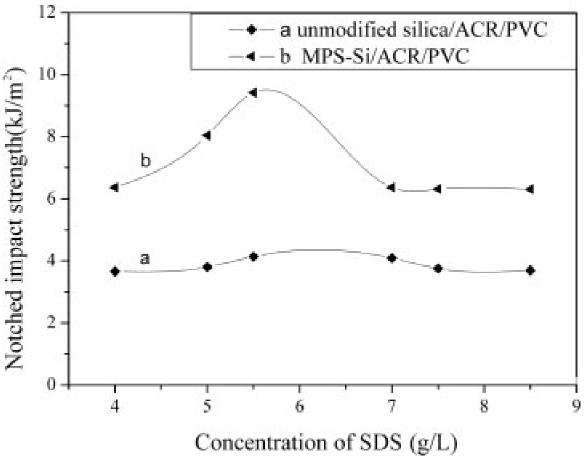


Figure 10 The curve of the notched impact strength of MPS-Si/ACR/PVC blends versus the SDS concentration.

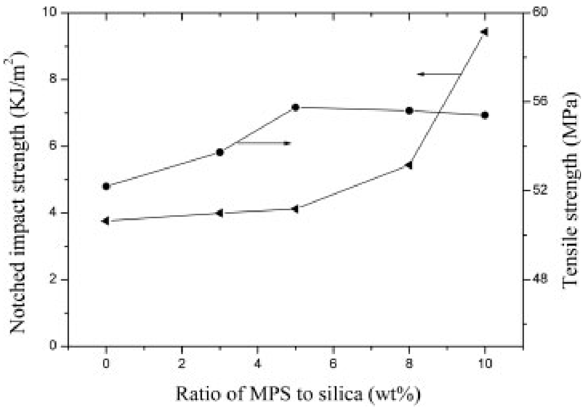
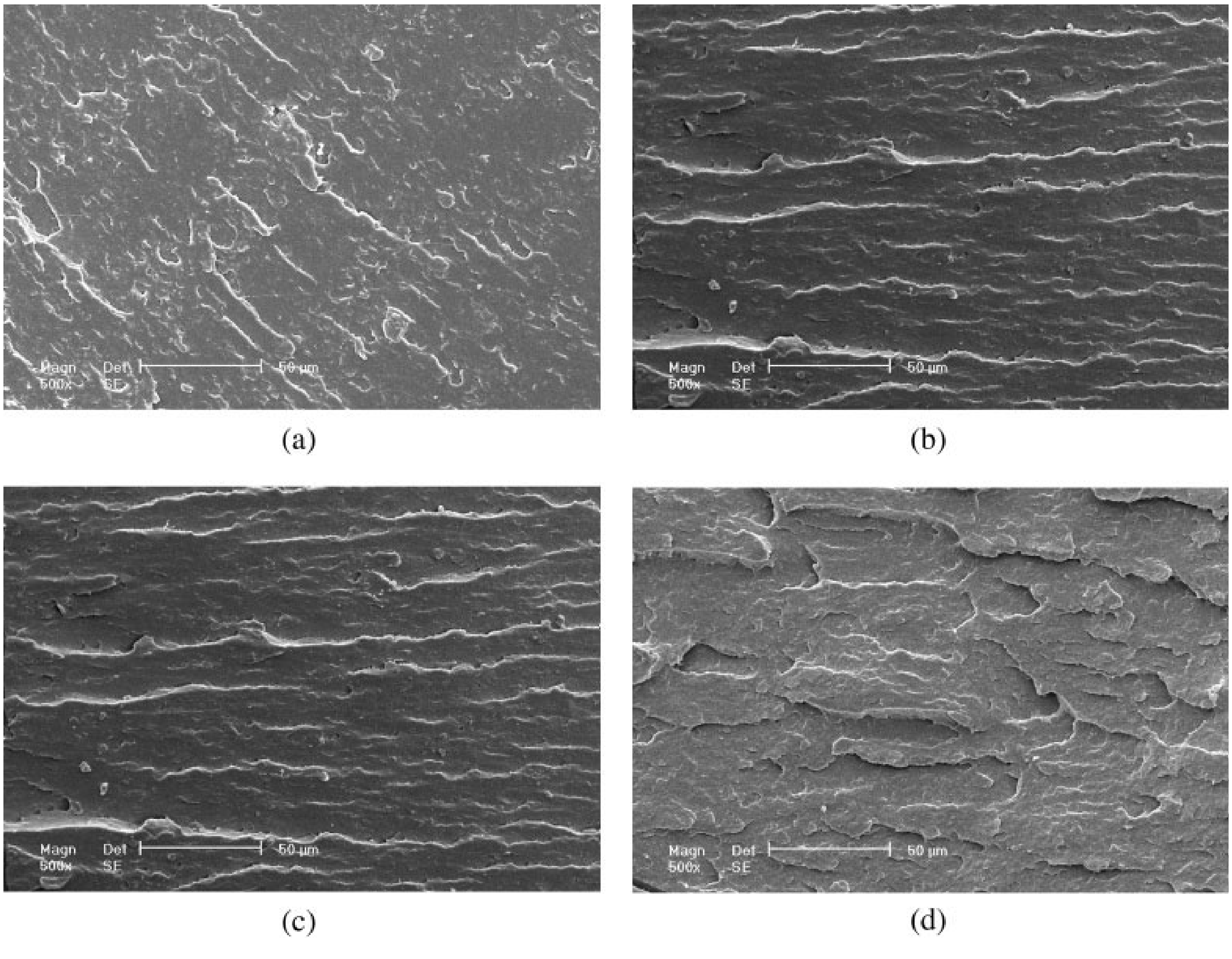


Figure 11 The curve of the mechanical properties of MPS-Si/ACR/PVC blends versus the weight ratios of MPS to silica.

emulsifier used to prepare the MPS-Si/ACR composite latexes when the concentration was under 5.5 g/L, while decreased above 5.5 g/L, as shown in Figure 10(b). It is believed that the features of the filler-matrix interfacial layer were responsible to a great extent for the impact properties of polymer matrix. When unmodified silicas were added to PVC matrix, a mild change in the impact strength was measured regardless of the emulsifier concentration being low or high, shown in Figure 10(a). It could be attributed to the worse dispersion of nanosilicas in the PVC matrix. The loosened clusters of the nanosilicas were surely detrimental to the impact toughness of the blends. It had been known that diameter size decreased with the increase of the emulsifier concentration as described above. Only did the particle sizes for the rubber components reach an optimal value, could the rubber particles play a toughening effect on the PVC matrix. It was bad for the rubber particles to produce cavitation capacity and yielding for the matrix when their particle sizes were too small. The notched impact strength achieved to 9.43 kJ/m^2 at 5.5 g/L concentration of SDS, which was about three times as much as that of pure PVC (3.13 kJ/m^2).

The notched impact strength was improved rapidly when the ratio of MPS to silica was above 5 wt %, as shown in Figure 11, while the tensile strength



(a) (b) (c) (d)

Figure 12 SEM microphotographs of fractured surface of PVC blends with different contents of MPS-Si/ACR (g/100 g PVC), (a) pure PVC, (b) 2 g, (c) 4 g, (d) 6 g.

increased slightly, and then a slow decrease. This was due to the fact that the silica particles had high modulus and tensile strength. At the interface of the MPS-Si/ACR and the PVC matrix, a thick gradient layer could be formed and provide an effective bridge for the matrix to pass the stress to the inorganic particles. Thus, the tensile strength could be improved.[41] When the ratios of MPS to silica were over 5 wt %, the thicker gradient layer around the nanosilicas would hinder the separation of nanosilicas agglomerate in the matrix polymer. Meanwhile, the influence of the ratio of MPS to silica on the Charpy impact strength of PVC matrix was rather significant. This suggested that for the blends subjected to impact loading, the interfacial regions were able to resist crack propagation more effectively than the polymer matrix. The use of rigid inorganic filler particles in a polymer matrix under tension would cause stress concentrations followed by debonding and shear yielding which were found to be deformation mechanisms in PVC. Obviously the higher the resistance to separation between matrix and MPS-Si/ACR composite particles, the higher the stresses that could be applied to the specimen before the separation took place.

SEM microphotographs of fractured surface of the blends

We examined the notched impact fractured morphology of pure PVC and different emulsifier concentrations of MPS-silica/ACR/PVC blends by SEM, as shown in Figure 12(a–d). For the pure PVC, it could be seen from Figure 12(a) that there were many cavities leading to brittle failure. For the other samples mixed with MPS-Si/ACR composite particles, the PVC matrices were severely deformed and drawn around the particles, as in Figures 12(b–d), because silane coupling agent (MPS) was grafted on the surface of silica and PMMA shell was covered on the surface of the nanosilica latex particles.[42,43] These led to increasing the interaction between the nanosilica particles and PVC matrix, thus enhanced their dispersion in the PVC matrix and improved the tensile strength and impact strength for the large energy absorption of the blends.

CONCLUSIONS

The morphology, the grafting ratio, and zeta potentials of the modified nanosilicas with methacryloxypropyltrimethoxysilane (MPS) were affected by the pH value, and the weight ratio of MPS to silica and reaction time. A high grafting ratio could be reached with proper reaction conditions. The synthesized MPS-silica/PBA/PMMA core-shell latices (MPS-Si/ACR) were used to toughen the PVC matrix. The MPS-Si/ACR/PVC blends had significant toughening effect compared with the unmodified silicas because of the good dispersion and good adhesive interface between silica and ACR in PVC matrix. Concentration of SDS, the content of MPS-Si/ACR particles, and the weight ratio of MPS to silica also influenced the mechanical properties of MPS-Si/ACR/PVC blends.

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