

The effect of octamethylcyclotetrasiloxane (D₄) addition on the structure and properties of film-forming polyacrylate/silica core-shell composite particles

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ABSTRACT: The film-forming polyacrylate/silica core-shell nanocomposite particles with octamethylcyclotetrasiloxane (D₄) were successfully synthesized via aqueous emulsion polymerization in the presence of a glycerol-functionalized nano silica sol. The ring-opening polymerization of D₄ and the reaction with the glycerol-functionalized nano silica particles before emulsion polymerization was the key procedure in this process. Transmission electron microscopy results showed that more nano silica particles tended to coat on the polyacrylate particles surface after the nano silica sols were modified with D₄. The silica aggregation efficiency was increased from 90.9 to 98.6% when the amount of D₄ used in the system was varied from 0 to 8.0 wt %. The transparency of the nanocomposite films was not compromised after D₄ was incorporated into the system. The films of the nanocomposite particles with or without D₄ both exhibited superior abrasive resistance. Furthermore, the water resistance and hydrophobicity of the films of these particles with D₄ were also improved significantly. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42003.

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INTRODUCTION

Nanocomposite particles composed of silica and polymer have been extensively studied recently due to their superior thermal, mechanical, optical and electrical properties, which derive from the synergy between the two components.^{1,2} Polymer/silica nanocomposite particles with various structures and morphologies such as hollow, core-shell, asymmetric and raspberry-like have been successfully fabricated. These nanocomposite particles can be applied in exterior facade coatings, adhesives, electronics, catalysis and diagnostics.³

Polymer/silica core-shell nanocomposite particles are usually prepared through miniemulsion polymerization^{4–6} or emulsion polymerization route. For example, Zhou *et al.*⁵ synthesized a series of poly(styrene-co-butyl acrylate)/SiO₂ nanocomposite microspheres with various morphologies including multicore-shell, core-shell, and raspberry-like structures via miniemulsion polymerization. However, the surfactants used in the (mini)emulsion polymerization system jeopardize many properties of polymer latex film, such as hydrophobicity, water resistance, surface adhesion, and weatherability. Newly developed surfactant-free emulsion polymerization approach is able to solve these problems by getting rid of surfactants in a synthesis

recipe. The research pioneers successfully made use of vinylpyridine as an auxiliary monomer with other vinyl monomers to prepare polymer/silica core-shell nanocomposite particles via this surfactant-free emulsion polymerization approach in the presence of ultrafine aqueous silica sol as the acid-base interaction between hydroxyl groups of silica surface and amino groups of vinylpyridine was active enough for the bonding of organic and inorganic phases.^{7–17} Recently, a highly efficient route to prepare vinyl (co)polymer-silica nanocomposite colloidal particles was reported by Armes and his coworkers.^{18–22} Colloidally stable polystyrene/silica and poly-(styrene-co-*n*-butyl acrylate)/silica core-shell nanocomposite particles of around 200–400 nm in diameter containing 22–28 wt % silica can be readily prepared by aqueous emulsion polymerization with glycerol-functionalized ultrafine aqueous silica sols in the absence of any surfactant, auxiliary comonomer, or cosolvent. High silica aggregation efficiency (up to 95%) was achieved.

As it has been reported in the references, high silica aggregation efficiency (>95%) could be achieved when glycerol-functionalized nano silica sols were used for preparing polymer/silica core-shell nanocomposite particles especially for poly(methyl methacrylate) (PMMA)/silica and polystyrene (PS)/silica nanocomposite particles.^{19,20} However, the silica

aggregation efficiency of polymer/silica core-shell nanocomposite particles was found decreased significantly for the copolymerization system of methyl methacrylate (MMA) and *n*-butyl acrylate (BA). For instance, the silica aggregation efficiency was below 70% (determined by thermogravimetric analysis) when a 50 : 50 mass ratio of MMA and *n*-BA was designed for the copolymerization. This issue had to be addressed, as the uncombined or free nano silica sols existing in the solution could adversely affect the application properties of such nanocomposite particles. For instance, the excess silica could compromise the stimulus-responsive property of Pickering emulsifiers.¹⁹ Moreover, it is difficult to elaborate the relationship between the structure and the properties of the nanocomposite materials when excessive nano silica sols exist in the system. The normal procedure to remove these free nano silica particles by centrifugation and re-dispersion is quite time consuming, and the low efficiency of silica utilization is not economic either. Therefore, how to increase silica aggregation efficiency of poly (MMA-*co*-BA)/silica nanocomposite particles is of great importance for a better implementation of these nanocomposite particles in various applications.

In current work, an improved formulation to prepare film-forming core-shell poly (MMA-*co*-BA)/silica nanocomposite particles for high silica aggregation efficiency is reported. Octamethylcyclotetrasiloxane (D₄) was introduced to modify glycerol-functionalized nano silica sols before aqueous emulsion copolymerization. Silicone polymers are of high scientific and technological interest owing to their unique characteristics such as high flexibility, excellent thermal stability, high gas permeability, and low surface energy. There are increasing interests to incorporate polysiloxane polymers into film-forming polyacrylic lattices to combine the advantages of silicone polymers and film-forming polyacrylic lattices.²⁵ As is well known, D₄ is a type of cyclosiloxane which is used to produce polydimethylsiloxane (PDMS) via ring-open polymerization. PDMS possesses many excellent properties such as high flexibility and hydrophobicity, low glass transition temperature and surface free energy, good weather and chemical resistance, excellent thermal stability, and biocompatibility.^{23,24} In the last decade, there have been increasing studies focusing on synthesis PDMS/polyacrylate nanocomposite particles.^{25–27}

In this article, a series of poly (MMA-*co*-BA)/silica particles have been synthesized by aqueous emulsion copolymerization in the presence of a glycerol-functionalized nano silica sol which was modified with different amount of D₄. The effect of addition method and the amount of D₄ added on the structure of the nanocomposite particles and the properties of the film formed by these nanocomposite particles are investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BA) were purchased from Sinopharm Chemical Reagent, and passed through an alkaline alumina column to remove inhibitor before using. Octamethylcyclotetrasiloxane (D₄) was obtained from Dow Corning Corporation. Hydrochloric acid (HCl, 38 wt %) and ammonia (NH₃·H₂O, 28 wt %) were also purchased from

Sinopharm Chemical Reagent and used as received without further treatment. 2,2'-Azobis(isobutyramidine) dihydrochloride (AIBA) was used as received from Aladdin reagent. Nano silica sol (CC30; 30 wt % aqueous dispersion; 7 nm nominal diameter) was supplied by Huipu Chemical. Deionized water was used in all experiments.

Synthesis of Polyacrylate/Silica Core-Shell Nanocomposite Particles with D₄

A typical process for preparation of nanocomposite particles was as follows: 10.0 g of glycerol-functionalized nano silica sol CC30, 30.0 g of deionized water and a certain amount of D₄ were mixed together and added into a three-neck round-bottomed flask. Then HCl was dropped into the flask and adjusted the pH value of the mixture to approximate 1 under stirring. Afterwards, the mixture was bubbled with nitrogen for 30 min to remove oxygen. Then the mixture was heated to 70°C and maintained for 3 h. The mixture was followed by the addition of 150 mg of AIBA initiator dissolved in 5.0 g of deionized water. Then, the mixture of MMA (2.5 g) and BA (2.5 g) was added into the flask at the same time. The polymerization was allowed to proceed for 24 h under a nitrogen atmosphere. Finally, the obtained emulsion was cooled to room temperature and the pH value of the final emulsion was adjusted to be 7.0–8.0 with ammonia. The amount of D₄ was varied from 0.1 g (1.2 wt %) to 0.7 g (8.0 wt %) systematically to investigate its effects on the structure and properties of nanocomposite particles. A control experiment was carried out by conducting a reaction without D₄.

Characterization of Polyacrylate/Silica Core-Shell Nanocomposite Particles and Films with D₄

Particles Size and Distribution. Dynamic light scattering (DLS, Malvern Zetasizer NanoZS Instrument) was used to obtain intensity-average hydrodynamic particle diameters and the distribution of nanocomposite particles by analyzing the scattered light at 90°C.

Silica Aggregation Efficiency. Silica aggregation efficiency was determined by centrifugation of the latex at 10,000 rpm for 30 min, followed by gravimetric analysis of the solid content of the supernatant.

The silica aggregation efficiency is determined as follows:

Silica aggregation efficiency = (30% – solid content of the supernatant)/30% × 100%.

Transmission Electron Microscope (TEM). The morphologies of the nanocomposite particles were characterized by TEM (Hitachi JEM-2100F Instrument at 200 kV). The emulsion was diluted with deionized water and dropped on to the carbon-coated copper grid for TEM observation.

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR was applied to characterize the chemical structures of the nanocomposite particles. The specimens were dried at 100°C for 24 h to remove water and residual monomer.

Ultraviolet Visible (UV-Vis) Spectra. The transmission spectra of the films with a mean thickness of 60 μm in the wavelength range of 350–800 nm were recorded on a UV-vis

spectrophotometer (Hitachi UV4100 instrument). The scanning speed was set as 300 nm/min. About 0.2 g of emulsion was coated on a glass slide of 9 cm² at 35°C to form a smooth and transparent film. Then the nanocomposite film with glass slide was dried in an oven at 100°C for 24 h.

Water Uptake Property. Water uptake ratio of the nanocomposite films at various immersion times was measured. First of all, the film specimen was prepared as the process mentioned above. Afterwards, the specimen was put into deionized water for different periods and taken out to weigh. The free water on the films was gently wiped-off before weighing every time. The water content of the film is determined as follows:

$$\text{Water content (wt \%)} = [(W_1 - W_0)/W_0] \times 100\%$$

W_0 is the mass of the initial dry film mass with the glass slide; W_1 is the mass of the film with glass slide soaked in solution for a certain time.

The appearance change of the films was observed by naked eyes after the samples were soaked for 24 h. Water uptake was defined as weight increase relative to the initial mass of the film after a period of 24 h soaking.

Contact Angle Measurement. The hydrophobicity of the nanocomposite films was determined by static contact angle measurements (Dataphysics OCA200 contact angle system). A 2 μ L drop of deionized water was placed on the surface of a nanocomposite film coated on the glass slide. Photographs of the samples were then taken with computer software. The contact angle of the water droplet on the surface of the film was measured. The film specimen was prepared as the process mentioned above.

Abrasion Resistance Properties. The abrasion resistance performance of the films was determined by an abraser (Shanghai Modern Environmental Engineering Technology JM-IV instrument), using 1000 g balance weights. Approximately 2.0 g of emulsion was cast on the glass slide to form a film at 30°C. The specimens were rotated for 50 cycles first and another 1000 cycles afterwards.

$$\text{Abrasion weight loss} = m_1 - m_2$$

whereas m_1 and m_2 are the specimen weights after 50 cycles and 1000 cycles rotation, respectively.

The photographs were taken with photograph Canon IXUS 155 camera.

RESULTS AND DISCUSSION

Effects of D₄ Addition Method on the Synthesis of Polyacrylate/Silica Core-Shell Nanocomposite Particles

Two different D₄ addition methods were used to prepare core-shell polyacrylate/silica nanocomposite particles. For the first method, MMA and BA were added into the system first and polymerized in the presence of a glycerol-functionalized nano silica sol for 3 h and polyacrylate/silica core-shell particles were formed. Then D₄ was added into the polymerization system.

The properties of the latex and films fabricated by the method above were acceptable when the amount of D₄ was below

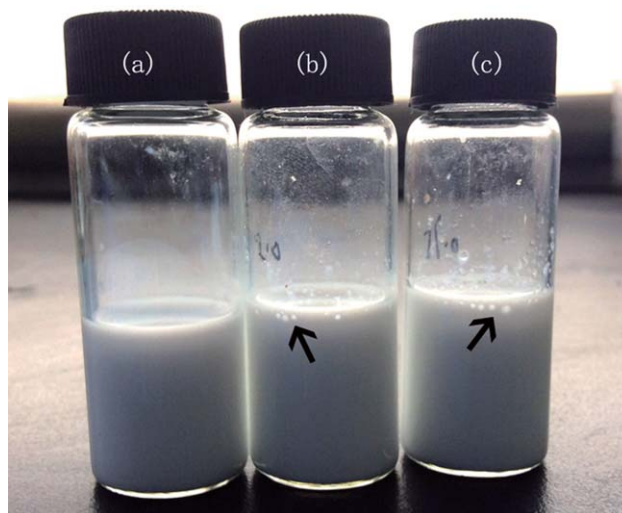


Figure 1. Appearance of the latex synthesized by two different D₄ addition methods (a) 0.70 g (8.0 wt %) of D₄ added before the monomers were polymerized. (b) 0.50 g (5.9 wt %) of D₄ added after the monomers were polymerized. (c) 0.75 g (8.6 wt %) of D₄ added after the monomers were polymerized. The black arrows point out the unreacted D₄ droplets. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.25 g. However, some tiny transparent oily D₄ droplets were found floating on the surface of white latex as the addition amount of D₄ exceeded 0.50 g, as shown in Figure 1. The D₄ droplets mixed in the emulsion would evaporate during film-forming process, leaving air bubbles and hollows within the films. This phenomenon indicated that the total conversion of D₄ was relatively low. The monomer conversion of the latex with 0.50 g (5.9 wt %) and 0.75 g (8.6 wt %) D₄ were only 96.4 and 95.3%, respectively, which were lower compared to that of latex synthesized through second D₄ addition method (>97.6%, as listed in Table I). In the first addition method, the polymerization reaction had been conducted for 3 h and most silica particles had aggregated within the polymer before D₄ was added to the system. Most of the silica particles were combined with polymer core as the shell of the composite particles. The specific surface area and the Si—OH groups of silica decreased dramatically. Therefore, the reaction probability between silica particles and D₄ monomer reduced which caused the low conversion of D₄. Besides, there was no extra surfactant in the system. The decrease of free silica particles caused the emulsifying capacity decline of the silica sol, causing a poor compatibility of D₄ and the emulsion, which also inhibited the interaction between D₄ and silica particles.

In the second addition method, D₄ was added before polyacrylate/silica nanocomposite particles were formed in an attempt to enhance the conversion of D₄. Feeding D₄ in the acidic silica sol without the presence of other monomers resulted in a more efficient ring-open polymerization of D₄. There were no visible transparent droplets existing in the latex even when the amount of D₄ added in the system was up to 0.70 g or 8.0 wt % (Figure 1), and the resulting film-forming properties of the latex were outstanding. The improvement of D₄ conversion suggested D₄ had reacted with silica particles efficiently. And the emulsify

Table I. Effect of Varying the D_4 Amount on the Particle Diameter, Monomer Conversion (Including D_4) and Silica Aggregation Efficiency of Polyacrylate/Silica Nanocomposite Particles

Initial D_4 amount (g)	Intensity-average diameter by DLS (nm)	Particle distribution index (PDI)	Silica aggregation efficiency (%)	Monomer conversion [including D_4 (%)]
0	208	0.079	90.9	98.1
0.20 (2.4 wt %)	190	0.020	92.3	98.5
0.40 (4.8 wt %)	219	0.104	94.0	97.6
0.60 (7.0 wt %)	231	0.088	98.3	98.2
0.70 (8.0 wt %)	207	0.098	98.6	97.8

capacity of silica sol also improved the compatibility between D_4 and the aqueous phase to some degree. Therefore in the following experiments, the second D_4 addition method was adopted to carry out the emulsion polymerization.

Morphologies and Structures of Polyacrylate/Silica Core–Shell Nanocomposite Particles with or without D_4

The morphologies of polyacrylate/silica nanocomposite particles with different D_4 loading are shown in Figure 2. It can be

observed that the polymer cores are not fully coated by silica particles and a lot of nano silica particles are dispersed on the background of the TEM images when the nanocomposite particles were fabricated without D_4 , as displayed in Figure 2(a). There is a noticeable decrease for the amount of uncombined nano silica particles at the background of TEM image when 0.2 g (2.4 wt %) D_4 was added into the system, as shown in Figure 2(b). Furthermore, the amount of free nano silica particles on the background become less and less when the amount

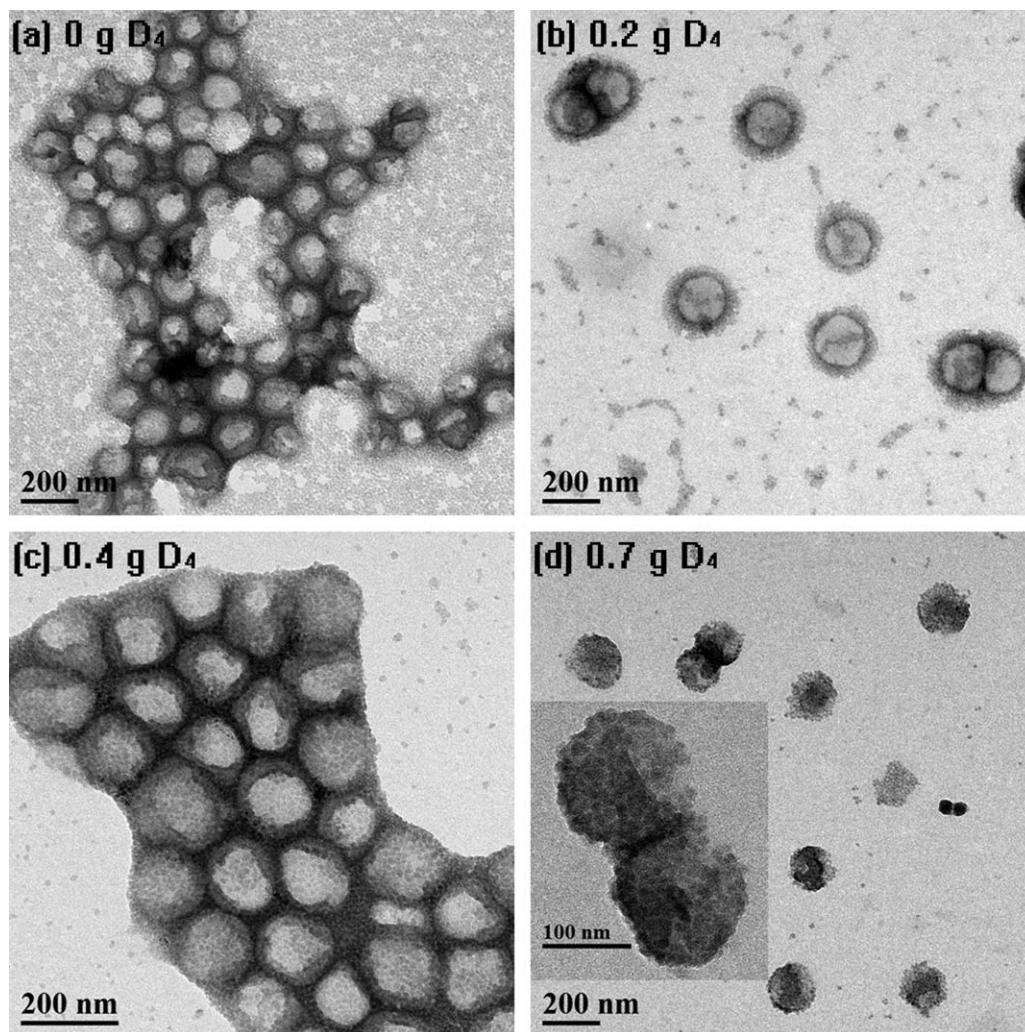


Figure 2. The TEM images of polyacrylate/silica core–shell nanocomposite particles with (a) 0 g, (b) 0.2 g (2.4 wt %), (c) 0.4 g (4.8 wt %), and (d) 0.7 g (8.0 wt %) D_4 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

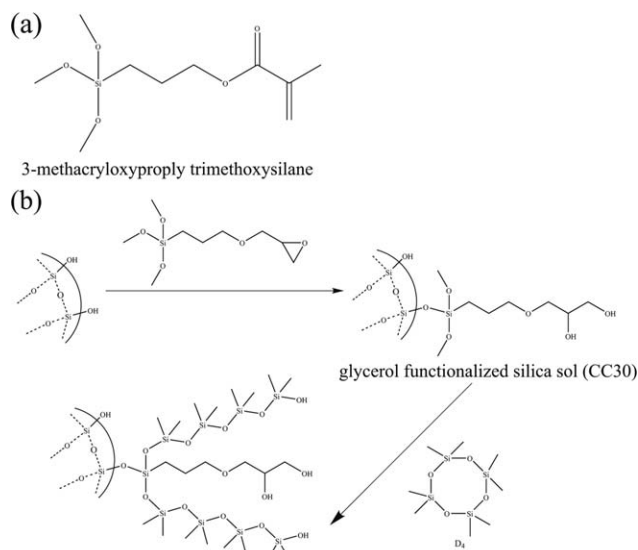


Figure 3. The structures of (a) 3-glycidoxypropyl trimethoxysilane; (b) schematic diagram of the reaction between D_4 and the glycerol functionalized silica sol.

of D_4 was increased [Figure 2(b–d)]. The results illustrated that the addition of D_4 was helpful to enhance the nano silica aggregated on the surface of nanocomposite particles. The silica aggregation efficiency calculated from the centrifugation results was improved from 90.9% to over 98.6% when the amount of D_4 added into the system was changed from 0 to 0.70 g (8.0 wt %). The application of D_4 in the system is very effective on improving the incorporation of nano silica with nanocomposite particles.

The glycerol functionalized silica sol (CC30) is manufactured by reacting the surface silanol groups of a conventional silica sol with 3-glycidoxypropyl trimethoxysilane.^{22,28} The chemical structure of 3-glycidoxypropyl trimethoxysilane was shown in Figure 3(a). Ring-opening reaction of the glycidyl group occurred simultaneously with the hydrolysis of the siloxane groups to produce a highly hydrophobic glycerol group. The Si–OH groups or Si–O–CH₃ groups of the surface of glycerol functionalized silica sol could react with D_4 , as displayed in Figure 3(b). The reaction between D_4 and Si–O–CH₃ or Si–OH groups on the surface of nano silica rendered the nano silica more hydrophobic and resulted in a better compatibility with the comonomers of MMA and BA for the Pickering emulsion polymerization, which led to the more aggregated structure nanocomposite particles, as displayed in Figure 2.

Particles Size and Distribution of Polyacrylate/Silica Core–Shell Nanocomposite Particles with and without D_4

The particle size and distribution of nanocomposite particles with various content of D_4 are shown in Table I. The intensity-average diameter of polyacrylate/silica nanocomposite particles without D_4 is 208 nm. For the polyacrylate/silica nanocomposite particles with D_4 , the particle sizes are range from 190 to 231 nm. The particle distribution index (PDI) of all nanocomposite particles is below 0.2, suggesting that the size distribution of all the nanocomposite particles is good. It seems that the

addition of D_4 does not play an important role on the particles size and distribution.

FT–IR Analysis Polyacrylate/Silica Core–Shell Nanocomposite Particles with and without D_4

Figure 4 presents the FT-IR spectra of polyacrylate/silica core-shell composite latexes with different loading of D_4 . In the spectrum of nanocomposite particles without D_4 , as shown in Figure 4(a), the bands at 2960, 2876, and 1731 nm are associated with the characteristic vibration of methyl (CH₃), methylene (CH₂), and carbonyl (C=O), respectively. There are three bands at 1000–1200 nm, corresponding to the vibration absorption of Si–O–Si, which is completely attributed to the inorganic silica.²¹ In the spectra of nanocomposite particles with 0.2 (2.4 wt %) and 0.7 g (8.0 wt %) D_4 [Figure 3(b,c)], compared to the spectrum of Figure 3(a), the three distinct bands at 1000–1200 nm became one wide bond at 1000–1300 nm, as the characteristic vibration band of Si–C is at about 1220–1260n,^{23,27} which means the characteristic bonds of Si–C and Si–O–Si have been mixed and covered each other and became one wide band. The differences of three spectra suggest that D_4 has been bonded to the silica surface by cationic ring-opening polymerization.

Optical Transparency of Polyacrylate/Silica Core–Shell Nanocomposite Particles Films with and without D_4

It is widely accepted that both the low silica aggregation efficiency and the poor compatibility between polysiloxane and polyacrylate would compromise the optical transparency of the polyacrylate/silica or polysiloxane-modified polyacrylate composite films.²⁰ Figure 5 shows that there was no significant change between the optical transparency properties of the polyacrylate/silica composite particles films with or without D_4 in the visible region. Nor were there obvious differences of the transparency properties with different content of D_4 in the nanocomposite film system. Transmission ratio for all the composite films exceeded 95% over the 350–800 nm range (visible

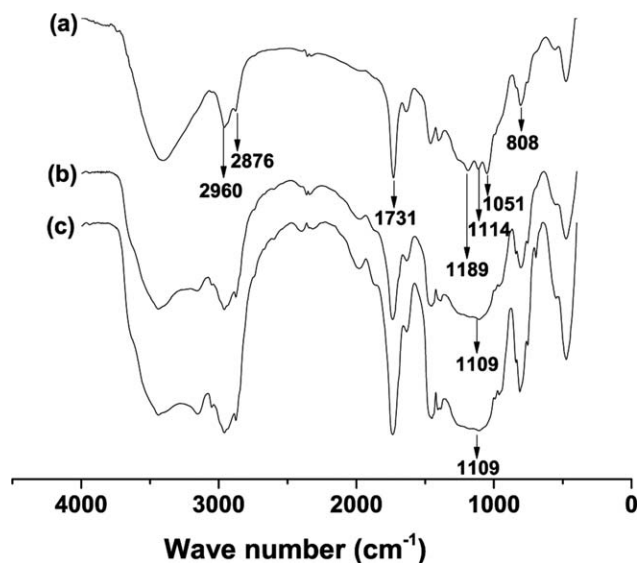


Figure 4. FT-IR spectra of polyacrylate/silica core-shell nanocomposite particles with (a) 0 g D_4 , (b) 0.2 g (2.4 wt %) D_4 , and (c) 0.7 g (8.0 wt %) D_4 .

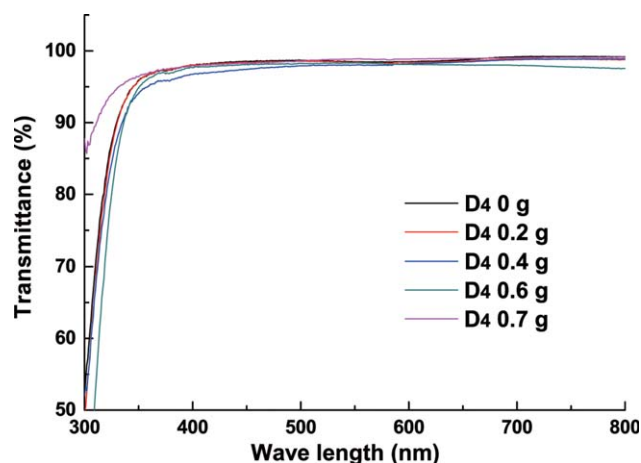


Figure 5. UV-vis transmittance spectra of polyacrylate/silica core-shell nanocomposite films at different content of D_4 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range). These excellent optical transparency properties indicated that the silica particles were homogeneously dispersed in the polymer.

Hydrophobicity of Polyacrylate/Silica Core-Shell Nanocomposite Films with and without D_4

The water repellent methyl groups along the main chain leads to the high hydrophobicity and low surface energy of PDMS. While the water contact angle has commonly been used as a criterion for the evaluation of hydrophobicity of a solid surface.²³ The results of static contact angle measurements results showed

that the hydrophobicity of the films was significantly improved after D_4 was incorporated into polyacrylate/silica nanocomposite particles. Figure 6 shows the images of water contact angle of the nanocomposite films with various loading content of D_4 . It can be observed that the hydrophobicity of the film was increased with increasing the contents of D_4 . The contact angle of the film without D_4 was only 56° , as shown in Figure 6(a), and it was increased to 82° after 0.7 g (8.0 wt %) D_4 was incorporated into the nanocomposite particle films, as displayed in Figure 6(d). This improvement on the hydrophobicity of the films resulted from the ring-opening polymerization of D_4 onto the surface of the nano silica. The Si-CH₃ of the PDMS led to a more hydrophobic surface of the core-shell polyacrylate/silica nanocomposite particles, as shown in Figure 3(b).

Water Resistance of Polyacrylate/Silica Core-Shell Nanocomposite Films with and without D_4

All the films with different content of D_4 were transparent, smooth and crack-free before the soaking process. After soaking them for 24 h in deionized water, the nanocomposite films with different loading of D_4 formed at 35°C exhibited distinct differences, as shown in Figure 7. The film without D_4 had been completely exfoliated from the glass slide and was so fragile that it was splintered into pieces as the water was wiped off after soaking for 24 h. The films of the nanocomposite particles with 0.1 g (1.2 wt %) and 0.2 g (2.4 wt %) of D_4 were also stripped off the glass slides but most of them still maintained the original shape after being soaked for 24 h. The nanocomposite particles films with 0.3–0.7 g (3.6–8.0 wt %) D_4 retained on the glass slides. The films looked the same as before the soaking.

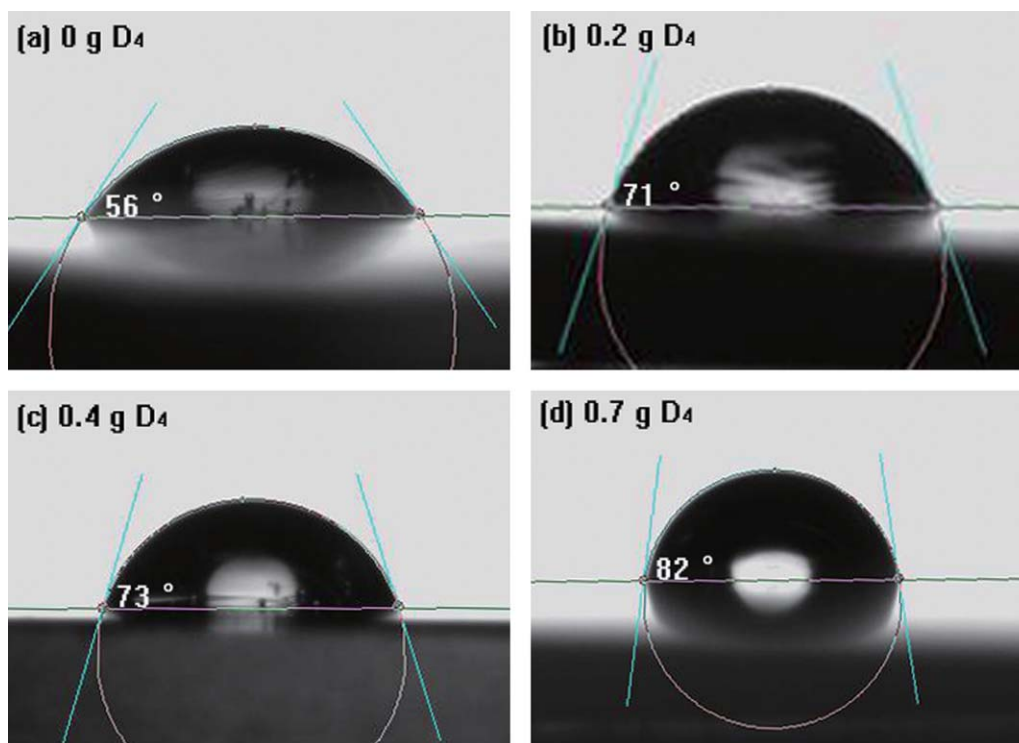


Figure 6. Static contact angle of polyacrylate/silica core-shell nanocomposite films with (a) 0 g, (b) 0.2 g (2.4 wt %), (c) 0.4 g (4.8 wt %), and (d) 0.7 g (8.0 wt %) D_4 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

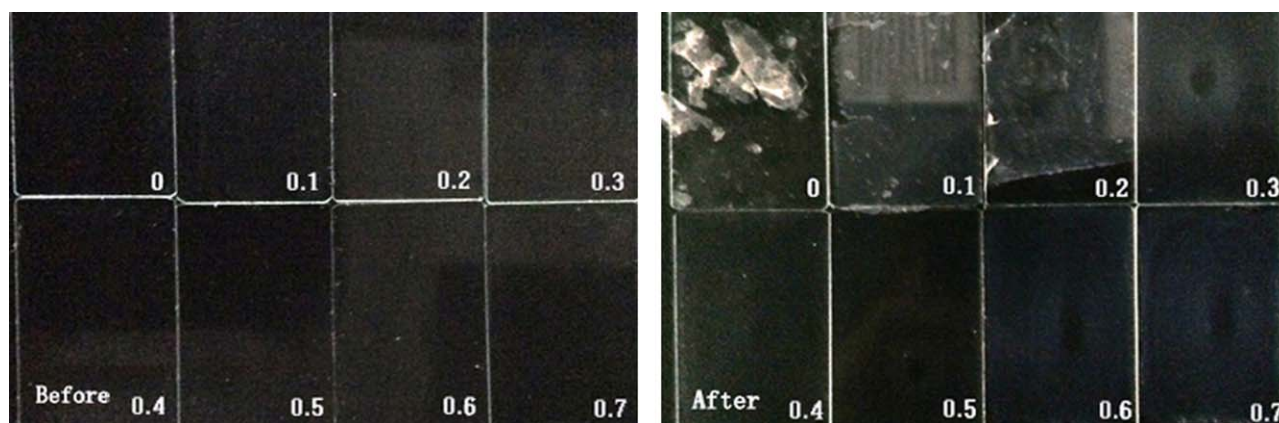


Figure 7. Polyacrylate/silica core-shell nanocomposite films before (left) and after (right) 24 h soaking process [numbers are initial D_4 mass (g)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

There was significant blushing for the film with 0.3 g (3.6 wt %) D_4 while the films with over 0.4 g (4.8 wt %) of D_4 exhibited good appearance after the 24 h soaking and almost no changes were observed from the films. It confirmed the films with D_4 possessed more hydrophobic surfaces and presented better water resistance. Moreover, the surfaces of nanocomposite particles were full of inorganic silica without D_4 added into the system. The polymer in the nanocomposite particles core was difficult to diffuse out of the shell and formed continuous film. Therefore, the interaction force between nanocomposite particles was rather poor, which resulted in the brittleness of the films. As D_4 was added into the system, the long PDMS chains were formed on the surface of silica/PA composite particles. The PDMS long chain could be entangled with each other during the film-forming process and enhanced the interaction force between nanocomposite particles. Therefore, the stickiness and flexibility of the films had been improved, and there were no splintering or exfoliation after 24 h soaking.

The changes of water absorption of the films with different loading of D_4 at different time are shown in Figure 8. The water uptake ratio of all the films was increased with time from 0 to

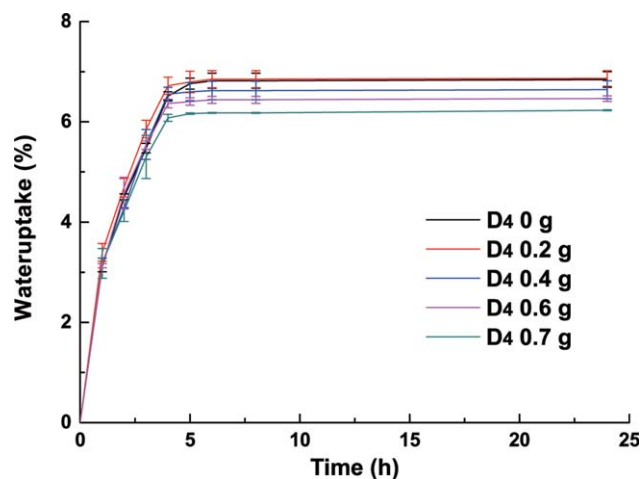


Figure 8. Wateruptake of polyacrylate/silica core-shell nanocomposite films with and without D_4 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

5 h and then showed no obvious change for the following time. The water absorption amounts of all the films were relatively low after soaking for 24 h (5–7%). The addition of D_4 hardly had any improvement on the water uptake of the nanocomposite particles films.

Abrasion Resistance Performance of Polyacrylate/Silica Core-Shell Nanocomposite Films with and without D_4

The abrasion resistance performance of all nanocomposite films was excellent. The weight losses were all below 0.030 g after 1000 cycles of abrasion with 1 kg loading, as shown in Figure 9. The abrasion resistance performance was improved slightly for the polyacrylate/silica nanocomposite films with D_4 , which resulted from the outstanding wear and durability of silicon. However, the improvement was limited because polyacrylate/silica nanocomposite without D_4 already showed excellent abrasion resistance performance (mass loss 0.024 g) compared to the literature.^{25,29} There was not much potential to improve for the abrasion resistance performance even if D_4 was added to the system. And the results confirmed the assumption. Furthermore, the amount of D_4 added into the system was limited.

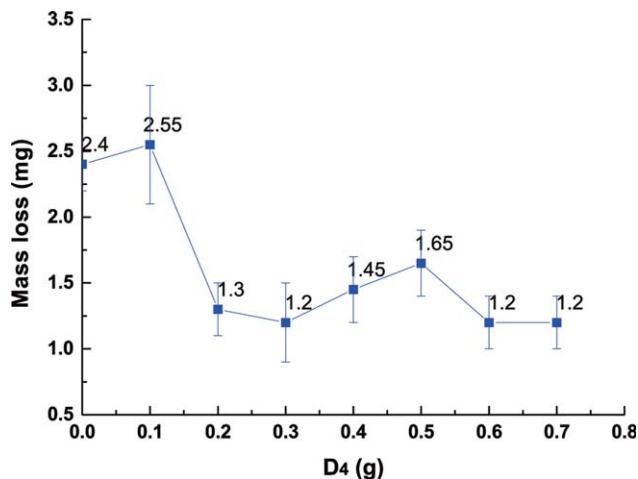


Figure 9. Weight loss of polyacrylate/silica core-shell nanocomposite films after 1000 cycles' rotation on an abramer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

The core-shell polyacrylate/silica nanocomposite particles with D₄ addition were successfully synthesized via aqueous soap free emulsion copolymerization in the presence of a nano silica sol. Compared to the polyacrylate/silica particles without D₄, higher silica aggregation can be achieved by adding D₄ to the polymerization system. The prepolymerization of D₄ with a silica sol before acrylate comonomers were added into the system was crucial for successful synthesis of polyacrylate/silica nanocomposite particles with D₄. There were significant improvements on the water resistance and hydrophobicity of the films after D₄ was incorporated into the nanocomposite particles. Furthermore, the films also showed excellent abrasion performance and optical transparency properties. This nanocomposite particles emulsion can be applied in many areas especially exterior facade coatings.

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