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Yuzuo Ye[a]; Xingrong Zeng[a]; Hongqiang Li[a]; Pingxu Chen[a]; Chaoxian Ye[a]; Fuchun Zhao[a]
[a] College of Materials Science and Engineering, South China University of Technology, Guangzhou, People's Republic of China

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Synthesis and Characterization of Nano-silica/Polyacrylate Composite Emulsions by Sol-gel Method and *in-situ* Emulsion Polymerization

YUZUO YE, XINGRONG ZENG*, HONGQIANG LI, PINGXU CHEN, CHAOXIAN YE
and FUCHUN ZHAO

College of Materials Science and Engineering, South China University of Technology, Guangzhou, People's Republic of China

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Organic nano-silica was firstly synthesized by sol-gel method with methyl methacrylate (MMA) and butyl acrylate (BA) in the micelles as dispersing media, tetraethoxysilicate (TEOS) as precursor, hydrochloric acid as catalyst and methacryloylpropyl trimethoxysilane (A174) as modifier. Subsequently, the nano-silica/polyacrylate composite emulsions were directly prepared by *in-situ* emulsion polymerization under the action of the initiator. The structure and properties were characterized by Fourier transform infrared spectroscopy (FTIR), dynamic light-scattering (DSL), thermogracvimetry (TG) and transmission electron microscopy (TEM). The results showed that A174-modified nano-silica was successfully synthesized in the acrylate-based emulsions by the sol-gel method. The nano-silica was encapsulated by polyacrylate, and the composite latex particles exhibited an apparent core-shell structure. The A174 could improve the lipophilicity of nano-silica and increase the grafting efficiency of polyacrylate on nano-silica particles. The nano-silica/polyacrylate composite latex film had better thermal stability, and the composite latex particles had greater average size and broader size distribution in contrast to those of pure polyacrylate emulsions.

Keywords: Nano-silica, composite emulsions, sol-gel method, *in situ* emulsion polymerization

1 Introduction

In recent years, the inorganic-organic composite emulsions have attracted much academic and industrial attention in the field of material science, due to the mild reaction conditions, low pollution and excellent overall properties including mechanical property, thermal property and even optical, electric, magnetic, catalytic properties, etc (1–4). The inorganic nanoparticles applied to polymers mainly include nano-silica, nano-titania, nano-calcium carbonate and nano-alumina (5–8). Among these inorganic nanoparticles, nano-silica is the most widely used in emulsions for its improvement of emulsions in mechanical, thermal properties and water-resistance (9). For example, Qi et al. (10) used the commercial nano-silica dispersions treated with methacryloylpropyl trimethoxysilane to synthesized acrylate polymer/nano-silica composite particles through miniemulsion polymerization. Zhang et al. (11) reported that the stability of emulsion polymerization was influenced by the amount of nano-silica particles, hydroxyethyl methacrylate (HEMA) and reaction temperature. Freris et al. (12) prepared nano-silica by Stöber method and applied it in the emulsion polymerization to obtain polymer encapsulation of nano-silica particles.

However, most literature reported that nano-silica/polyacrylate composite emulsions were synthesized with the available nano-silica or the nano-silica prepared by sol-gel method in ethanol as dispersing media (13, 14). These kinds of nano-silica should be redispersed in acrylate before polymerization. Furthermore, the nano-silica was especially easily to aggregate to bigger particles, and even form impurity in the process of the modification of nano-silica and the preparation of nano-silica/polyacrylate composite emulsions.

In this study, organic nano-silica was prepared by a sol-gel method in the acrylate-based emulsions, and the nano-silica-containing emulsions were applied in *in-situ* emulsion polymerization to synthesize nano-silica/polyacrylate composite emulsions. The structure and properties were investigated by Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), dynamic light-scattering (DLS), and transmission electron microscopy (TEM), and

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*Address correspondence to: Xingrong Zeng, College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China. E-mail: psxrzeng@gmail.com

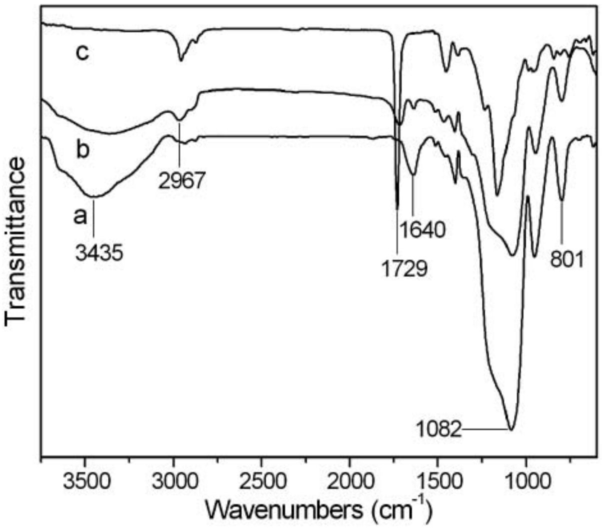

Fig. 1. FTIR spectra of (a) unmodified nano-silica, (b) A174-modified nano-silica and (c) nano-silica/polyacrylate composite latex film.

the formation mechanism of nano-silica/polyacrylate composite latex particles was also discussed.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA) were purchased from Tianjing Fuchen Chemical Reagents Factory, China. Tetraethoxysilicate (TEOS) was purchased from Tianjin No.1 Chemical Reagent Factory, China. Methacryloylpropyl trimethoxysilane (A174) was purchased from GE Co. Ltd., America. Ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) (DNS-86) was supplied by Qingxin Hanerchem Chemical Technology Co. Ltd., China and acted as emulsifier. Hydrochloric acid, ethanol, acetone and potassium persulfate (KPS) were all purchased from Guangdong Guanghua Chemical Factory Co. Ltd., China. All reagents were used as received without further purification.

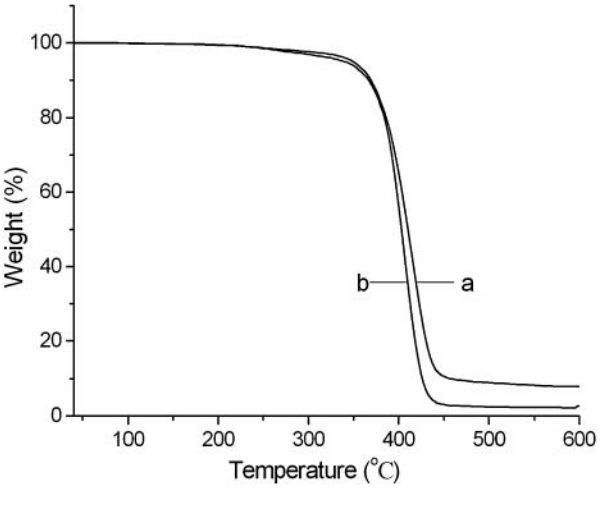

Fig. 2. TG curves of (a) nano-silca/polyacrylate composite latex film and (b) pure polyacrylate latex film.

Table 1. TG result of nano-silica/polyacrylate composite latex film and pure polyacrylate latex film

Samples	T_{onset}(°C)	T_{max}(°C)	T_{end}(°C)	W_{600}(%)
nano-silca /polyacrylate	381	417	436	7.9
pure polyacrylate	381	407	426	2.1

T_{onset} is the onset temperature of thermal decomposition; T_{max} is the temperature at the maximum rate of weight loss. T_{end} is the end temperature of thermal decomposition. W_{600} is the residue yield at 600°C.

2.2 Synthesis of Nano-silica/polyacrylate Composite Emulsions

The nano-silica/polyacrylate composite emulsions were prepared through a two-step procedure, which was described as follows.

A174 and TEOS with the molar ratio from 0:1 to 1:6 were mixed to 18 g of MMA and 18 g of BA. Then, the mixture was added to a solution of 3.6 g of DNS-86 and 0.18 g of hydrochloric acid in 40 g of deionized water, under gentle stirring at room temperature for 12 h. The organic nano-silica was prepared in the acrylate-based emulsions.

A quarter of the nano-silica-containing emulsions and 0.22 g of KPS dissolved in 15 g of deionized water were added to a 250 ml four-neck round bottom flask included 40 g of deionized water equipped with a mechanical stirrer, a reflux condenser and a thermometer at 75°C and reacted for 20 min, and the residual of nano-silica-containing emulsions was dropped into the system in 1 h and kept for 30 min. Afterwards, 67.4 g of pre-emulsions included MMA, BA, AA, DNS-86 and deionized water (the mass ratio of 1:1:0.06:0.015:2) and 0.22 g of KPS dissolved in 15 g of deionized water were added dropwise in 1.5 h. After the addition, the system was heated to 80°C and kept for 2 h. Then, it was cooled to room temperature to obtain the nano-silica/polyacrylate composite emulsions.

2.3 Characterization

Fourier transform infrared (FTIR) spectroscopy was carried out by Tensor27 (Bucker Company, Germany) to characterize nano-silica, organic nano-silica and nano-silica/polyacrylate composite latex film. The nano-silica-containing emulsions were vacuum dried at 30°C for 24 h to obtain the organic nano-silica powder. And then, the organic nano-silica powder was extracted by ethanol for

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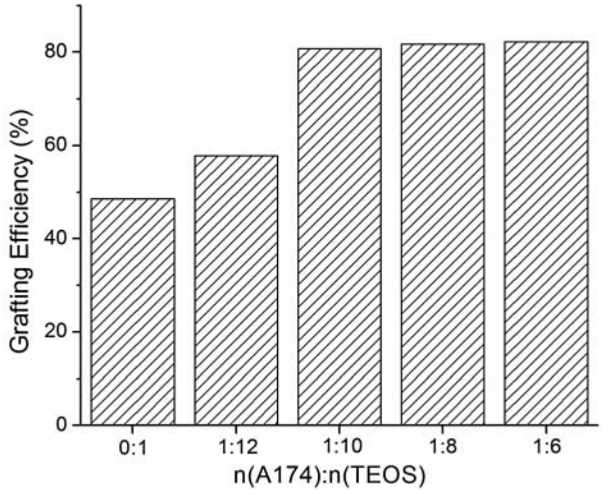

Fig. 3. Effect of the molar ratio of A174 to TEOS on the grafting efficiency of polyacrylate.

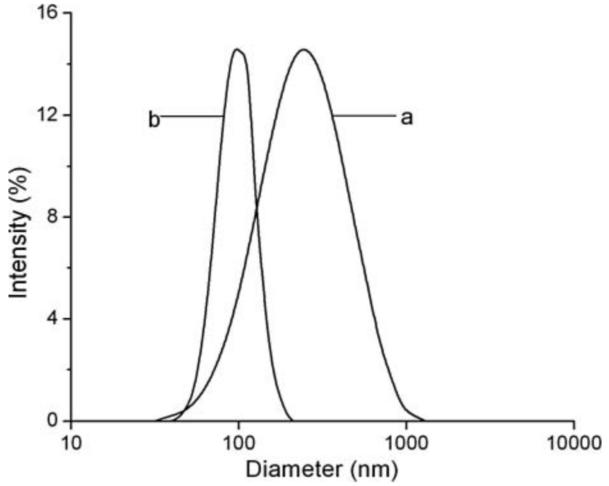

Fig. 4. Curves of the size and its distribution of (a) nano-silca/polyacrylate composite latex particles and (b) pure polyacrylate latex particles.

24 h to remove the emulsifier and the free A174. The same method was used to separate and purify the nano-silica powder. Nano-silica/polyacrylate composite latex film was extracted by acetone for 24 h to remove pure polyacrylate.

Dynamic light-scattering (DSL) analysis was used to investigate the size and distribution of nano-silica/polyacrylate composite latex particles and pure polyacrylate latex particles by Mastersizer 2000 E (Malvern Instruments Ltd., UK).

The transmission electron microscope (TEM) images of nano-silica/polyacrylate composite latex particles and pure polyacrylate latex particles were recorded on a Tecnai 12 (FEI, Netherlands). The emulsions were diluted, dried on carbon-coated copper grids, and stained by phosphate-tungstic acid.

Thermogravimetry (TG) analysis was used to examine the thermal stability of nano-silica/polyacrylate composite latex film by TG 209 (Netzsch Company, Germany). The specimens were heated from 50°C to 600°C at a heating rate of $20^\circ\mathrm{C} \cdot \mathrm{min}^{-1}$ under nitrogen.

The grafting efficiency of polyacrylate on nano-silica was defined as the weight percentage of grafted polyacrylate on the surface of nano-silica to the total polyacrylate. Nano-silica/polyacrylate composite emulsions of different surface modified degrees of nano-silica were dried and extracted by acetone for 24 h to remove pure polyacrylate. The grafting efficiency of polyacrylate on nano-silica was calculated as the following equation (15):

$$\text{Grafting Efficiency} = \frac{m_1 - m_2}{m_0 - m_2} \times 100\% \qquad (1)$$

Where m_0 is the weight of composite latex film before extraction; m_1 is the weight of composite latex film after extraction; m_2 is the weight of nano-silica in the composite latex film which the extracted composite latex film was heated at 800 °C for 3 h in muffle furnace.

3 Results and Discussion

3.1 FTIR Analysis

Figure 1 illustrates the FTIR spectra of unmodified nano-silica, A174-modified nano-silica and nano-silica/polyacrylate composite latex film. It can be seen that the characteristic adsorption peaks of nano-silica at about 1082 cm^{-1} and 801 cm^{-1} are assigned to the asymmetric and symmetric stretching vibration of Si-O-Si, respectively. The spectrum a and b show the adsorption bands at 3435 cm^{-1} and 1640 cm^{-1} attributed to the hydroxyl group on the surface of nano-silica. The appearance of the peaks at 1729 $\mathrm{cm}^{-1}$and 2967 cm^{-1} attributed to the vibration of C=O and the stretching adsorption of C-H, respectively, indicates that the surface of nano-silica is modified by A174 in the acrylate-based emulsions.

In spectrum c, the relative intensities of the adsorption at 1729 cm^{-1} and 2967 cm^{-1} attributed to the vibration of C=O and the stretching adsorption of C-H, respectively, are much stronger than those of spectrum b using the vibration of Si-O-Si at 1082 cm^{-1} as internal standard adsorption band, demonstrating that the acrylate monomers have been grafted on the nano-silica by A174. The adsorption peaks of OH at 3435 cm^{-1} and 1640 cm^{-1} disappear in contrast to spectrum b, indicating that nano-silica particles are well encapsulated by polyacrylate.

3.2 TG Analysis

Figure 2 and Table 1 show the TG curves and analysis result of nano-silica/polyacrylate composite latex film and pure polyacrylate latex film. The residue yield at 600°C of nano-silica/polyacrylate composite latex film is higher than that of pure polyacrylate latex film, indicating the nano-silica exists in the composite latex film. Although the nano-silica/polyacrylate composite latex film and pure

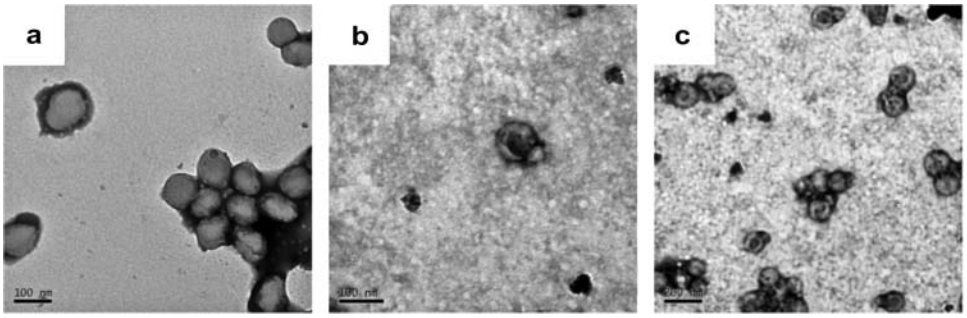

Fig. 5. TEM images of (a) pure polyacrylate latex particles (magnification 30,000), (b) nano-silica/polyacrylate composite latex particles (magnification 30,000), (c) nano-silica/polyacrylate composite latex particles (magnification 13,000).

polyacrylate latex film have the similar T_{onset} at about 381°C, T_{max} and T_{end} of the composite latex film is about 10°C higher than those of pure polyacrylate latex film. Based on the different decomposition behavior between the composite latex film and the pure latex film, the nano-silica encapsulated in polyacrylate can increase the thermal stability of polyacrylate, which is because the appropriate amount of nano-silica in the latex particles could restrict the transmission of the heat and protected the polyacrylate chains from breaking at a certain degree (16).

3.3 Effect of the Amount of A174 on the Grafting Efficiency of Polyacrylate

Figure 3 shows the effect of the amount of A174 on the grafting efficiency of polyacrylate. After the pure polyacrylate is extracted by acetone, there are no more than 50%

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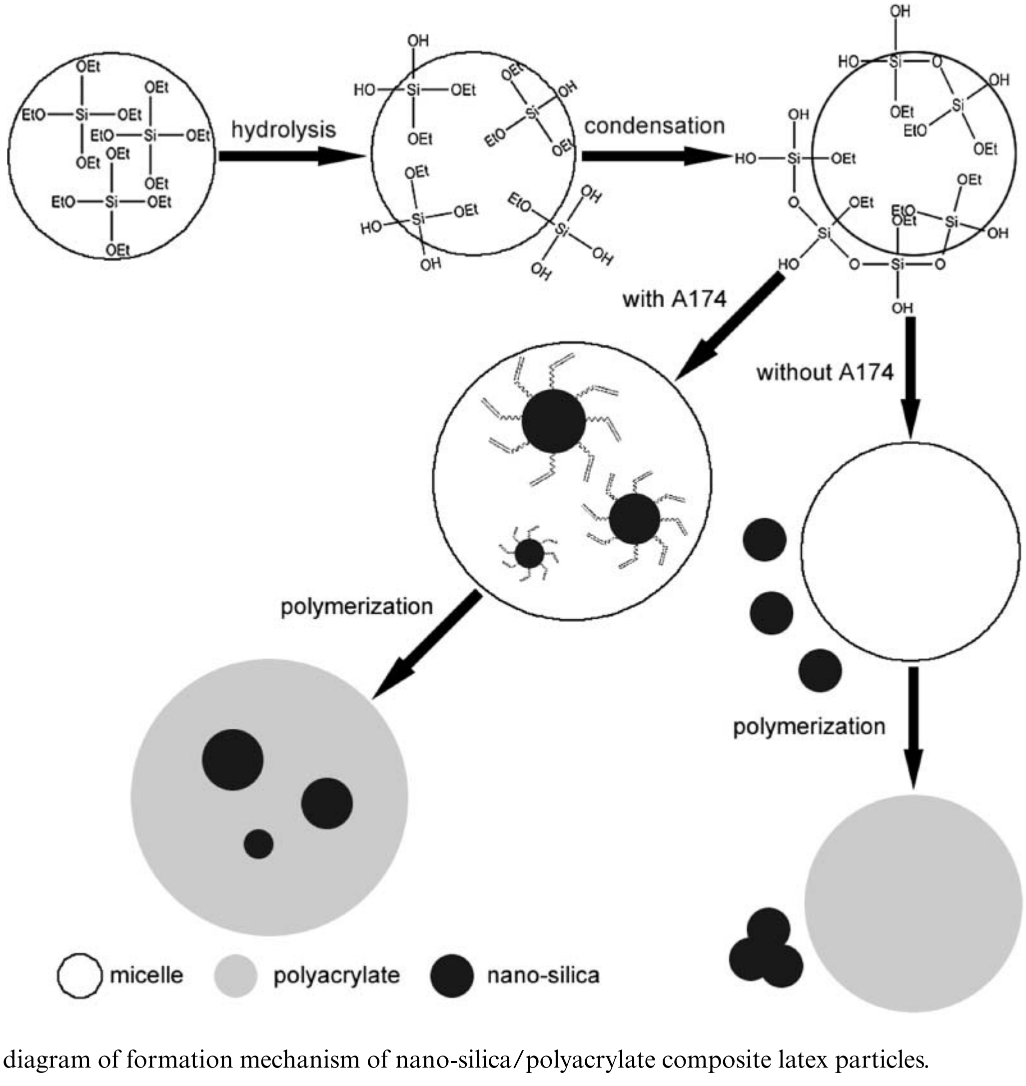

Fig. 6. Schematic diagram of formation mechanism of nano-silica/polyacrylate composite latex particles.

acrylate monomers that were grafted on the surface of unmodified silica, and the grafting efficiency of polyacrylate increases rapidly with the addition of A174. However, when the molar ratio of A174 to TEOS exceeds 1:10, the grafting efficiency levels off at about 80%. Therefore, the modification of A174 to nano-silica could strengthen the combination between nano-silica and polyacrylate.

3.4 DSL Analysis

Figure 4 shows the curves of the particle size and distribution of nano-silica/polyacrylate composite latex particles and pure polyacrylate latex particles. The particle size of nano-silica/polyacrylate composite latex particles increases and its distribution widens in contrast to those of pure polyacrylate latex particles. It indicates that nano-silica is encapsulated into polyacrylate, and more than one silica particle is encapsulated in a polyacrylate latex particle. Furthermore, a small amount of particles with smaller size than that of pure polyacrylate latex particles is observed in curve a, which can be explained that free unmodified nano-silica is not encapsulated.

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3.5 TEM Analysis

The morphology of nano-silica/polyacrylate composite latex particles and pure polyacrylate latex particles was observed by TEM, as shown in Figure 5. It can be seen that the composite latex particles are core-shell structure in image b and c compared with that in image a. The dark core is nano-silica, and its size distributes from 10 nm to 60 nm. The light layer encapsulating on the dark core is polyacrylate, which cannot be dyed by phosphate-tungstic acid. Furthermore, there is more than one nano-silica particle encapsulated into a polyacrylate latex particle. Except for encapsulated nano-silica, a small amount of free nano-silica also exists, and its size is about 30 nm. The TEM result is consistent with that of DSL analysis.

3.6 Formation Mechanism of Nano-Silica/Polyacrylate Composite Latex Particles

Figure 6 shows the schematic diagram of the formation mechanism of nano-silica/polyacrylate composite latex particles. In the mixture of the TEOS with monomer phase, hydrolysis takes place as a consequence of the contact with the aqueous phase. When hydrolysis proceeds, the SiOH-based molecule will become water soluble and hence, the condensation will occur in aqueous phase (17). However, with the addition of A174 into the system, the surface of nano-silica is functionalized by methacryloylpropyl groups, which would improve the lipophilicity of nano-silica and contain polymerizable carbon-carbon double bond. The organic nano-silica will be diverted into monomers or absorb the monomers on its surface. With the proceeding of *in situ* emulsion polymerization under the role of the initiator, the organic nano-silica is encapsulated in polyacrylate. Simultaneously, some unmodified nano-silica would agglomerate each other, due to its high surface energy (9).

4 Conclusions

A continuous preparation approach for nano-silica/polyacrylate composite emulsions was presented in our work. First, organic nano-silica was successfully prepared in the acrylate-based emulsions by sol-gel process. Subsequently, the nano-silica-containing emulsions were directly applied in *in situ* emulsion polymerization to synthesize nano-silica/polyacrylate composite emulsions. The composite latex particles exhibited multinuclear core-shell structure with nano-silica as the core and polyacrylate as the shell. The A174 used to modify the nano-silica could increase the grafting efficiency of polyacrylate on nano-silica. In comparison with pure polyacrylate, the nano-silica/polyacrylate composite latex film showed the better thermal stability, and the particle size of composite latex particles was greater and its distribution was broader.

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