Synthesis and Characterization of Film-forming Polymer/SiO₂ Nanocomposite *via* Surfactant-Free Emulsion Polymerization

QIANQIAN SHANG, HU LIU, LIJING GAO and GUOMIN XIAO*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P.R. China

*Corresponding author: Tel/Fax: +86 25 52090612; E-mail: xiaogm@seu.edu.cn

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Poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid)/SiO₂ (PMMA-BA-MAA)/SiO₂ nanocomposite particles were prepared *via* surfactant-free emulsion polymerization. The effects of SiO₂ content on the emulsion stability, monomer conversion and polymerization rate were investigated. The experimental results revealed that (PMMA-BA-MAA)/SiO₂ nanocomposite particles were film-forming and the polymer spheres with ordered arrangement structure were bounded by SiO₂ networks. SiO₂ particles (or aggregates), which had strong interaction with the polymer matrix, were enriched at the surface of the nanocomposite films. The dried nanocomposite films showed better water resistance than the pure polymer film and the film containing 10 wt % SiO₂ had the lowest water adsorption (0.070 g/g).

Key Words: Film-forming, Nanocomposite, Emulsion polymerization, SiO₂ particles, Acrylic polymer.

INTRODUCTION

The field of organic/inorganic nanocomposite materials is of growing interest, because they combine the properties of the polymer moiety with inorganic nanoparticles in an advantageous way, *e.g.*, amalgamating the flexibility, the toughness and the ability of the polymer to form films with the thermal stability and the mechanical strength of the inorganic nanoparticles¹⁻⁶. These materials are likely to become one of the fastest developing materials because of their extensive potential applications in various fields of material science, ranging from nanolithography², next-generation exterior facade paints³ and scratch-resistant transparent coatings⁴ to polymer light-emitting diodes⁵ and molecular imprinting⁶.

In the past decades, many methods have been developed to prepare organic/inorganic nanocomposite materials, such as sol-gel process^{7,8}, free-radical copolymerization^{9,10}, emulsion polymerization¹¹⁻¹⁵ and self-assembly methods¹⁶. Among these methods, emulsion polymerization has become the most frequently used technology, since its easy synthesis processes and good stability of polymer nanocomposite latex particles. An enormous variety of inorganic particles have been associated to nanocomposite materials, among which silica was the most intensively studied due to its high stability, high thermal resistance, electrical and optic properties, as well as its extensive applications in diverse areas¹⁷. Recently, many studies have been devoted to the preparation of organic/inorganic nanocomposites in the presence of SiO₂ particles.

For example, Qiao *et al.*¹⁸, presented a facile preparation approach for raspberry-like silica/polystyrene/silica multilayer nanocomposite particles *via* mini-emulsion polymerization. They used larger surface-modified SiO₂ as the core and smaller unmodified SiO₂ as the shell with 4-vinylpyridine as an auxiliary monomer. Guo *et al.*¹⁹, prepared MPS-nanosilica/acrylic core-shell composite latex and discussed its application in toughening PVC matrix. However, it seemed that the majority of these works were focused on the preparation of nanocomposites with the functional modified inorganic particles as the core in the presence of surfactant and only a few works were involved in the formation of nanocomposites by surfactant-free emulsion polymerization and the effect of the unmodified inorganic particles on the kinetics of the surfactant-free emulsion polymerization systems.

In this work, we introduced a novel method for the synthesis of film-forming poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid)/SiO₂ (PMMA-BA-MAA)/SiO₂ nanocomposite particles through surfactant-free emulsion polymerization with an ordered arrangement surface structure. The effects of SiO₂ content on the emulsion stability, monomer conversion and polymerization rate were investigated. The nanocomposite particles were dried to form nanocomposite films and the water resistance of the films was investigated.

EXPERIMENTAL

Tetraethoxysilane (TEOS), methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA) and ammonium

persulfate (APS) were purchased from Shanghai Lingfeng Chemical Reagent CO. Ltd., China. Methyl methacrylate and butyl acrylate were distilled to remove the inhibitor in vacuo and stored at 4 °C for use. The other materials were used as received. Deionized water was used in all experiments.

Preparation of SiO₂ nanoparticles: SiO₂ particles were synthesized by Stöber method²⁰. The reaction was carried out in a 500 mL three-neck round-bottom flask with a mixture of 300 mL ethanol and 25 mL aqueous solution of ammonia. The mixture was stirred vigorously to homogenize at room temperature. After stabilization, tetraethoxysilane (10 mL) was quickly added into the solution and the hydrolysis and condensation reaction occurred with continuous stirring for 36 h. The obtained SiO₂ particles were purified by centrifugation, decantation and resuspension in water with ultrasonic for three times.

Synthesis of nanocomposite particles: The nanocomposite particles were synthesized by the copolymerization of MMA, BA and MAA under aqueous conditions in the present of SiO₂ nanoparticles. The typical experimental process was as follows: SiO₂ particles (0.3 g), MMA (7.2 g), BA (4.8 g) and MAA (0.232 g, 2.7 mmol) were mixed with 100 mL water and then the mixture were placed into a 250 mL four-necked flask equipped with a reflux condenser, drop ping funnel, nitrogen gas inlet and a mechanical stirrer. After sufficiently degassed under stirring, the reactor was placed in a water bath at 75 °C. Then ammonium persulfate (APS) aqueous solution (0.12 g of APS was dissolved in 8 mL deionized water) was added to initiate emulsion polymerization. The reaction system was stirred at 75 °C for 4 h. The samples were taken out of the reactor at regular intervals to determine the monomer conversion after adding a drop of hydroquinone aqueous solution. The latex particles without SiO₂ nanoparticles were also prepared by surfactant-free emulsion polymerization using different dosages of MAA.

Fabrication of nanocomposite films: The nanocomposite films were fabricated by drop casting the nanocomposite emulsion on freshly cleaned glass substrates. First, the glass substrates were cleaned in detergent solution by sonication for 0.5 h and rinsed with water thoroughly. Then, as-prepared nanocomposite emulsion was carefully cast on this cleaned glass substrate and solvent was allowed to evaporate at 80 °C for 4 h.

Characterization: Monomer conversion (M) and solids concentration (S) were determined using the gravimetric method. Coagulum was filtered using a strainer, washed by water and dried to a constant weight at 80 °C. The dry mass of coagulum (m_c) and total emulsion mass (m_e) was measured and the coagulum concentration (C) was determined by the mass ratio of m_c and m_e . Fourier-transform infrared analyses

were conducted using a Nicolet 5700 Fourier-transform spectrometer in the range of 4000–400 cm⁻¹ at room temperature (Thermo Electron Corporation, America). Scanning electron microscopy (SEM, S-3000N, Hitach Company, Japan) was employed to characterize the morphologies of silica nanoparticles, nanocomposite latex particles and films. Water absorption of the films was determined by measuring the weight variation of films before and after being immersed into deionized water for 24 h at ambient temperature.

RESULTS AND DISCUSSION

Synthesis of (PMMA-BA-MAA)/SiO₂ nanocomposite particles: The surfactant-free emulsion polymerization was carried out at various MAA dosages and the effect of MAA on the monomer conversion and coagulum content was shown in Table-1. The coagulum content was used to evaluate the polymerization stability. The larger the value of coagulation content is, the worse the polymerization stability is. Since preliminary experiments without the addition of MAA led to unstable solution, MAA was added into the polymerizations. When 2.1–3.3 mmol of MAA was introduced, the emulsion polymerization processes were stable and the optimal amount of MAA was around 2.7 mmol, at which the monomer conversion was higher than 90 % and the coagulum content was lower than 1 %. With either less or more MAA, the monomer conversion decreased and the formation of the coagulum occurred. Therefore, we subsequently carried out the surfactant-free emulsion polymerization using 2.7 mmol MAA.

The effects of SiO₂ content on the solid content of the emulsion and the monomer conversion was investigated, as shown in Table-2. It could be seen that the solid content of the emulsion and the degree of monomer conversion increased when silica nanoparticles were added into the reaction system. This was because it was of benefit for the formation of hydrogen bonds between the silanol groups of the silica particles and the -COOH groups on the polymer particles surface under a acidic character of polymerization condition (pH = 2.5–5.5)²¹ via hydrogen bonds, the SiO₂ nanoparticles could enhance the stability of latex by providing the polymer latex particles with steric hindrance stabilization.

SEM image of SiO₂ nanoparticles was shown Fig. 1, which demonstrated that the as-prepared SiO₂ nanoparticles were uniformly spherical and highly monodisperse. The average diameter of SiO₂ nanoparticles determined by SEM was 60 nm. The relationship between SiO₂ content and the reaction rate was illustrated, as shown in Fig. 2. It was found that the reaction rate was accelerated and the monomer conversion was increased when SiO₂ nanoparticles were added. The initiate rate of polymerization in the present of SiO₂ particles was faster

TABLE-1
EFFECT OF MAA ON THE SURFACTANT-FREE EMULSION POLYMERIZATION

Run	MAA (mmol)	MMA (g)	BA (g)	APS (g)	Water (g)	S (%)	M (%)	C (%)
1	0	7.2	4.8	0.12	108	—	—	Agglomerating
2	2.1	7.2	4.8	0.12	108	7.86	78.7	8.56
3	2.4	7.2	4.8	0.12	108	8.59	85.8	0.37
4	2.7	7.2	4.8	0.12	108	9.04	90.7	0.24
5	3.0	7.2	4.8	0.12	108	8.04	80.0	1.44
6	3.3	7.2	4.8	0.12	108	7.38	73.3	6.32

TABLE-2
EFFECT OF SiO₂ CONTENT ON THE SURFACTANT-FREE EMULSION POLYMERIZATION

Run ^a	MAA (mmol)	SiO ₂ (g)	SiO ₂ content (%) ^b	S (%)	pH	M (%)
1	2.7	0	0	9.04	2.53	90.7
2	2.7	0.3	2.5	9.27	3.34	92.1
3	2.7	0.6	5	10.4	4.98	98.9
4	2.7	1.2	10	10.5	5.49	95.9

^a7.2 g MMA and 4.8 g BA were added in all runs. ^bBased on the total monomer weight.

Fig. 1. SEM image of the SiO₂ nanoparticles

Fig. 2. Effect of SiO₂ contents on the conversion *versus* time curves for emulsifier-free emulsion polymerization

than the system without SiO₂ and the reaction rate tended to become greater with the amount of SiO₂ up to 10 wt %. However, the monomer conversion was slightly reduced when SiO₂ content was higher than 5 wt %, since the nucleation was hindered by the possible aggregation of SiO₂ at a high concentration.

Fig. 3 showed the SEM images of the nanocomposite particles with different SiO₂ content. The polymer particles without SiO₂ were uniformly spherical (Fig. 3a). When SiO₂ were introduced into the reaction system, the polymer particles were bounded by SiO₂ rather than encapsulated SiO₂ particles into interior. At 2.5 wt % SiO₂ particles, superficial and inter-related SiO₂ networks were clearly seen on the film surface (Fig. 3b) and the polymer particles were embedded and somewhat orderly arrayed. As SiO₂ particles were increased to 5 wt %, smooth ordered film-forming nanocomposite particles

Fig. 3. SEM images for (PMMA-BA-MAA)/SiO₂ nanocomposite particles with different SiO₂ contents: a, 0 wt %; b, 2.5 wt %; c, 5 wt %; d, 10 wt %

could be obtained (Fig. 3c). Increasing the SiO₂ content up to 10 wt %, the aggregation of SiO₂ happened and the nanocomposite latex particles ordered arranged were locally destroyed (Fig. 3d). These results suggested that 5 wt % SiO₂ particles were already enough for the formation of an integrated SiO₂ network.

Morphology of (PMMA-BA-MAA)/SiO₂ nanocomposite films: The typical SEM images of the surface and cross-section of these nanocomposite films were demonstrated in Fig. 4. It could be seen that the surface of the film was rather smooth in the absence of SiO₂ particles. However, when the SiO₂ content increased to 5 or 10 wt %, particles *ca.* 200–400 nm brought by agglomeration of the SiO₂ particles were observable on the films surface, which indicated the nanocomposite films had silica-rich surfaces. The observation in the film cross-section indicated that the SiO₂ particles were implanted into the polymer matrix and kept the continuity and compactness of the film, which meant that there was a strong interaction between the SiO₂ particles and the polymer matrix.

Fig. 4. SEM images of (PMMA-BA-MAA)/SiO₂ nanocomposite films with different SiO₂ contents: a, surface, 0 wt %; b, surface, 5 wt %; c, surface, 10 wt %; d, cross-section, 10 wt %

The agglomeration of SiO₂ particles was mainly caused by the reason that the SiO₂ particles surrounded the polymer latex particles rather than within the polymer latex particles (Fig. 3b-d). During the formation stage of the nanocomposite films, these non-embraced SiO₂ particles preferentially surrounded polymer latex particles, then contacted with each other and further transformed into SiO₂ aggregates *via* condensation of silanol groups, accompanied with the evaporation of water.

Water resistance of (PMMA-BA-AA)/SiO₂ nanocomposite films: Water absorption amount of the nanocomposite films were investigated (Fig. 5). The pure (PMMA-BA-MAA) film had the highest water adsorption (0.143 g/g), while nanocomposite films showed lower water adsorption than it. The carboxyl groups on the surface of the pure (PMMA-BA-MAA) latex film made the film surface hydrophilic which caused the high water adsorption. In nanocomposite films, SiO₂ particles interacted with the polymer chains through hydrogen bonding between the silanol groups and the carbonyl groups and the SiO₂ particles aggregated with each other *via* the interaction of silanol groups. All these decreased the content of hydrophilic portion on the surfaces of nanocomposite films and made the surfaces more hydrophobic. Consequently, the amount of adsorbed water on the film surfaces decreased when the introduced SiO₂ particles were increased. The most SiO₂ aggregates were detected on the surface of the film containing 10 wt % SiO₂ particles (Fig. 5c); hence the nanocomposite film had the lowest water adsorption (0.070 g/g).

Fig. 5. Absorption amount of water of the nanocomposite films containing various contents of SiO₂ particles: a, 0 wt %; b, 2.5 wt %; c, 5 wt %; d, 10 wt %

Conclusion

The facile synthesis of novel film-forming (PMMA-BA-MAA)/SiO₂ nanocomposite particles by surfactant-free emulsion polymerization was described in this work. The research results demonstrated that the amount of MAA was very important to the monomer conversion and the SiO₂ particles could accelerate the polymerization rate and increase monomer

conversion at the dosage from 2.5-10 wt %. (PMMA-BA-MAA)/SiO₂ nanocomposite particles were proved to be film-forming and SEM results indicated the ordered arrangement of polymer spheres bounded by SiO₂ networks. Surface and cross-section morphology studies of the nanocomposite films suggested that SiO₂ particles were enriched at the film surface and they had strong interaction with the polymer matrix. Water resistance studies indicated that (PMMA-BA-MAA)/SiO₂ nanocomposite films showed better water resistance property compared with the pure polymer film and the amount of adsorbed water decreased along with the increasing of SiO₂ content. Thus the (PMMA-BA-MAA)/SiO₂ nanocomposite particles have potential applications in paints and coatings with good water repellency.

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