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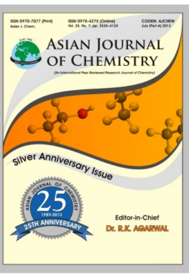

Synthesis and Characterization of Film-forming Polymer/SiO_2 Nanocomposite *via* Surfactant-Free Emulsion Polymerization

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Poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid)/SiO_2 (PMMA-BA-MAA)/SiO_2) nanocomposite particles were prepared *via* surfactant-free emulsion polymerization. The effects of SiO_2 content on the emulsion stability, monomer conversion and polymerization rate were investigated. The experimental results revealed that (PMMA-BA-MAA)/SiO_2 nanocomposite particles were film-forming and the polymer spheres with ordered arrangement structure were bounded by SiO_2 networks. SiO_2 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 % SiO_2 had the lowest water adsorption (0.070 g/g).

Key Words: Film-forming, Nanocomposite, Emulsion polymerization, SiO_2 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 nanoparticles[1-6]. 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 nanolithography[2], next-generation exterior facade paints[3] and scratch-resistant transparent coatings[4] to polymer light-emitting diodes[5] and molecular imprinting[6].

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 polymerization[11-15] and self-assembly methods[16]. 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 areas[17]. Recently, many studies have been devoted to the preparation of organic/inorganic nanocomposites in the presence of SiO_2 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 SiO_2 as the core and smaller unmodified SiO_2 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)/SiO_2 (PMMA-BA-MAA)/SiO_2) nanocomposite particles through surfactant-free emulsion polymerization with an ordered arrangement surface structure. The effects of SiO_2 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 ºC for use. The other materials were used as received. Deionized water was used in all experiments.

Preparation of SiO_2 nanoparticles: SiO_2 particles were synthesized by Stöber method[20]. 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 SiO_2 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 SiO_2 nanoparticles. The typical experimental process was as follows: SiO_2 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 ºC. 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 ºC 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 SiO_2 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 ºC 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 ºC. 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 immerged into deionized water for 24 h at ambient temperature.

RESULTS AND DISCUSSION

Synthesis of (PMMA-BA-MAA)/SiO_2 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 SiO_2 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 SiO_2 nanoparticles could enhance the stability of latex by providing the polymer latex particles with steric hindrance stabilization.

SEM image of SiO_2 nanoparticles was shown Fig. 1, which demonstrated that the as-prepared SiO_2 nanoparticles were uniformly spherical and highly monodisperse. The average diameter of SiO_2 nanoparticles determined by SEM was 60 nm. The relationship between SiO_2 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 SiO_2 nanoparticles were added. The initiate rate of polymerization in the present of SiO_2 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 SiO_2 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

[a] 7.2 g MMA and 4.8 g BA were added in all runs. [b] Based on the total monomer weight.

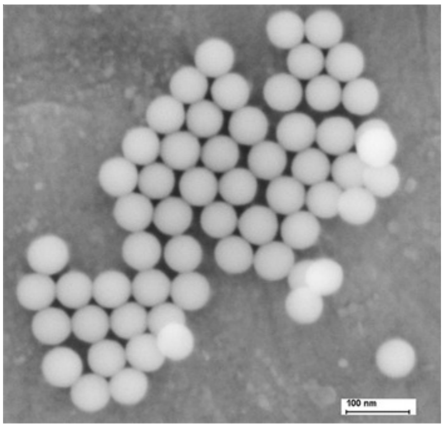

Fig. 1. SEM image of the SiO_2 nanoparticles

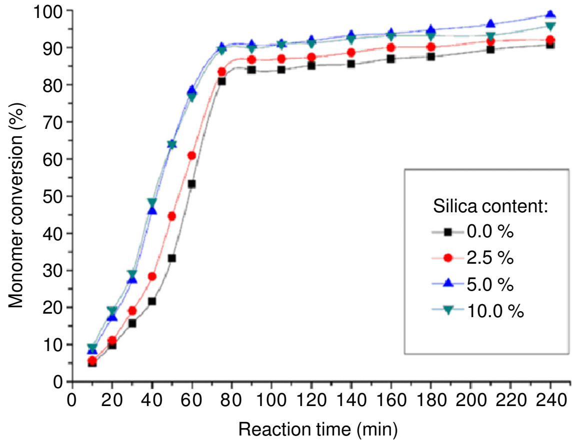

Fig. 2. Effect of SiO_2 contents on the conversion *versus* time curves for emulsifier-free emulsion polymerization

than the system without SiO_2 and the reaction rate tended to become greater with the amount of SiO_2 up to 10 wt %. However, the monomer conversion was slightly reduced when SiO_2 content was higher than 5 wt %, since the nucleation was hindered by the possible aggregation of SiO_2 at a high concentration.

Fig. 3 showed the SEM images of the nanocomposite particles with different SiO_2 content. The polymer particles without SiO_2 were uniformly spherical (Fig. 3a). When SiO_2 were introduced into the reaction system, the polymer particles were bounded by SiO_2 rather than encapsulated SiO_2 particles into interior. At 2.5 wt % SiO_2 particles, superficial and interrelated SiO_2 networks were clearly seen on the film surface (Fig. 3b) and the polymer particles were embedded and somewhat orderly arrayed. As SiO_2 particles were increased to 5 wt %, smooth ordered film-forming nanocomposite particles could be obtained (Fig. 3c). Increasing the SiO_2 content up to 10 wt %, the aggregation of SiO_2 happened and the nanocomposite latex particles ordered arranged were locally destroyed (Fig. 3d). These results suggested that 5 wt % SiO_2 particles were already enough for the formation of an integrated SiO_2 network.

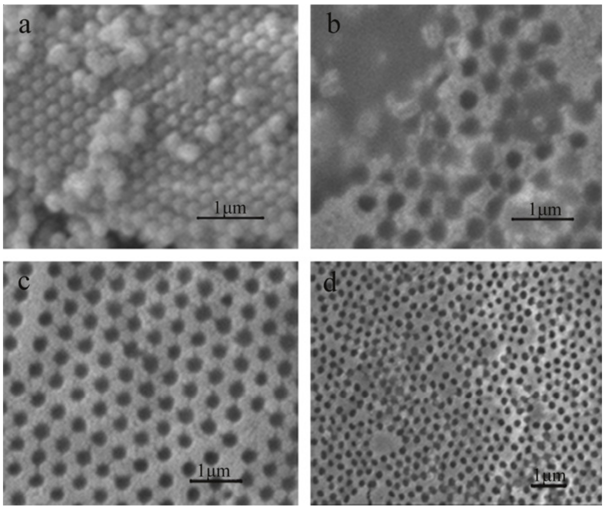

Fig. 3. SEM images for (PMMA-BA-MAA)/SiO_2 nanocomposite particles with different SiO_2 contents: a, 0 wt %; b, 2.5 wt %; c, 5 wt %; d, 10 wt %

Morphology of (PMMA-BA-MAA)/SiO_2 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 SiO_2 particles. However, when the SiO_2 content increased to 5 or 10 wt %, particles *ca*. 200-400 nm brought by agglomeration of the SiO_2 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 SiO_2 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 SiO_2 particles and the polymer matrix.

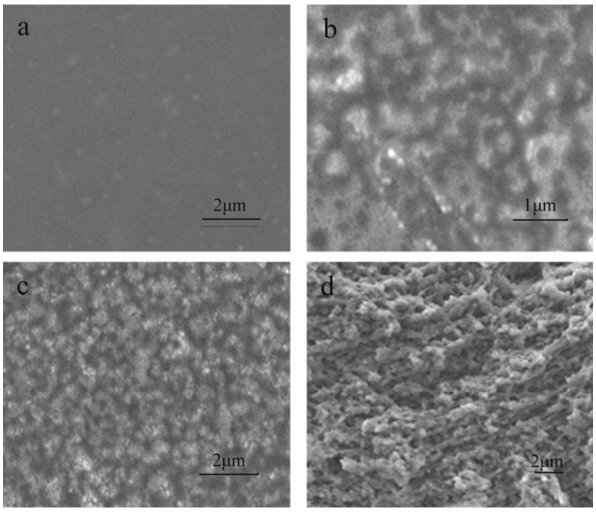

Fig. 4. SEM images of (PMMA-BA-MAA)/SiO_2 nanocomposite films with different SiO_2 contents: a, surface, 0 wt %; b, surface, 5 wt %; c, surface, 10 wt %; d, cross-section, 10 wt %

The agglomeration of SiO_2 particles was mainly caused by the reason that the SiO_2 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 SiO_2 particles preferentially surrounded polymer latex particles, then contacted with each other and further transformed into SiO_2 aggregates *via* condensation of silanol groups, accompanied with the evaporation of water.

Water resistance of (PMMA-BA-AA)/SiO_2 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, SiO_2 particles interacted with the polymer chains through hydrogen bonding between the silanol groups and the carbonyl groups and the SiO_2 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 SiO_2 particles were increased. The most SiO_2 aggregates were detected on the surface of the film containing 10 wt % SiO_2 particles (Fig. 5c); hence the nanocomposite film had the lowest water adsorption (0.070 g/g).

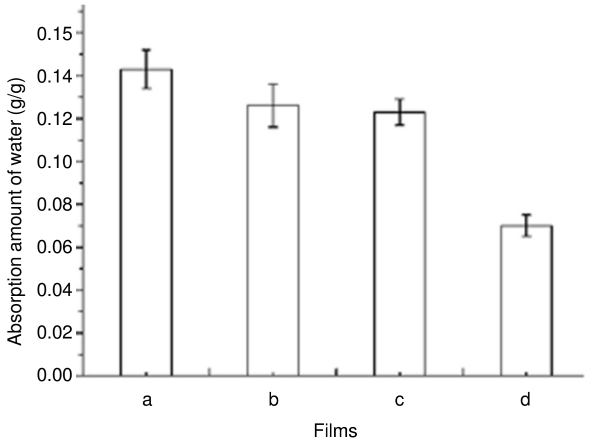

Fig. 5. Absorption amount of water of the nanocomposite films containing various contents of SiO_2 particles: a, 0 wt %; b, 2.5 wt %; c, 5 wt %; d, 10 wt %

Conclusion

The facile synthesis of novel film-forming (PMMA-BA-MAA)/SiO_2 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 SiO_2 particles could accelerate the polymerization rate and increase monomer conversion at the dosage from 2.5-10 wt %. (PMMA-BA-MAA)/SiO_2 nanocomposite particles were proved to be film-forming and SEM results indicated the ordered arrangement of polymer spheres bounded by SiO_2 networks. Surface and cross-section morphology studies of the nanocomposite films suggested that SiO_2 particles were enriched at the film surface and they had strong interaction with the polymer matrix. Water resistance studies indicated that (PMMA-BA-MAA)/SiO_2 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 SiO_2 content. Thus the (PMMA-BA-MAA)/SiO_2 nanocomposite particles have potential applications in paints and coatings with good water repellency.

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