Available online at www.sciencedirect.com

Polymer 47 (2006) 4622–4629

polymer

www.elsevier.com/locate/polymer

Preparation of acrylate polymer/silica nanocomposite particles with high silica encapsulation efficiency via miniemulsion polymerization

Dong-ming Qi, Yong-zhong Bao *, Zhi-xue Weng, Zhi-ming Huang

State Key Laboratory of Polymer Reaction Engineering, Department of Chemical Engineering, Zhejiang University, No. 38 Zheda Road, Hangzhou 310027, China

Received 28 November 2005; received in revised form 5 March 2006; accepted 10 April 2006
Available online 19 May 2006

Abstract

Acrylate polymer/silica nanocomposite particles were prepared through miniemulsion polymerization by using methyl methacrylate/butyl acrylate mixture containing the well-dispersed nano-sized silica particles coupling treated with 3-(trimethoxysilyl)propyl methacrylate (MPS). The encapsulation efficiency of silica particles was determined through the elution and hydrofluoride acid etching experiments, and the size distribution and the morphology of the composite latex particles were characterized by dynamic light scattering and transmission electron microscopy. The coupling treatment of silica with MPS can improve the encapsulation efficiency of silica and the degree of grafting of polymer onto silica. When 0.10 g MPS/g silica was used to modify silica, the encapsulation efficiency of silica was greater than 95%, and the degree of grafting of acrylate polymer onto silica was about 60%. Although the average size and the size distribution index of the composite latex particles increased as the weight fraction of silica increased, the stable latex containing the 'guava-like' composite particles was obtained. The grafting of polymer onto silica particles improved the dispersion of silica particles in the solvents for acrylate polymer and in the polymer matrix.

Keywords: Miniemulsion polymerization; Nanocomposite; Encapsulation

1. Introduction

In recent years, much attention has been paid to the preparation of polymer/nanometer-sized inorganic particles nanocomposites due to their attractive mechanical [1–4], thermal [5], optical [6,7], electrical [8], and magnetic [9] properties, and potential application in areas of plastics and rubber reinforcement, coatings, electronics, catalysis, and diagnostics.

The properties of nanocomposites are greatly influenced by both the dispersing degree of nano-particles in the base polymers and the interfacial adhesion between the inorganic and organic components. Although nanocomposites can be prepared by simply blending of nanoparticles with base polymers via high shear stirring or ball milling, the dispersing degree of nano-particles and the interfacial adhesion were obvious insufficient to obtain desirable material properties [10]. Therefore, many chemical approaches were developed for the preparation of nanocomposites in recent years.

Heterophase polymerization techniques seem to be ideal to achieve a well dispersion of nano-particles in the base polymers. By introducing coupling agents or reactive groups onto the surface of nanoparticles, a good interfacial adhesion between inorganic and organic components can also be achieved. In the heterophase polymerization techniques, the nanocomposites are formed by carrying out polymerization in the presence of inorganic particles via suspension [11], dispersion [12–14], emulsion [15–25] and miniemulsion processes [26–33]. Among these processes, emulsion polymerization is the most frequently used. By this process, the nanocomposite particles with core-shell [15–21], raspberry-like [22–24], daisy-shape, and multipod-like morphology [25] were obtained depending on the surface chemistry and the size of the inorganic particles. In emulsion polymerization, the principal locus of particle nucleation is either in the aqueous phase or in the monomer-swollen micelles. In the presence of inorganic particles in the aqueous phase, the particle surface can be an additional site for particle nucleation. Thus, the structure formation and morphology control of the nanocomposite particles can become heavily complicated due to the competition among these mechanisms.

The miniemulsion is a relatively stable oil-in-water dispersion, which is typically obtained by shearing a system containing monomer(s), water, surfactant and a costabilizer. The monomer droplets can range in diameter from 50 to

---

* Corresponding author. Tel./fax: +86 571 87951334.
E-mail addresses: yongzhongbao@zju.edu.cn, yongzhongbao@zj.com (Y.-z.Bao).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.04.024

500 nm. Because of their small size, the large overall surface area of the droplets can effectively compete for radical capture. As a result, monomer droplets in a miniemulsion become the dominant site for particle nucleation. If the inorganic particles could be dispersed in the monomer phase followed by minemulsification, each submicron droplet could indeed act as a nanoreactor, which produce nanocomposite particles with great encapsulation efficiencies of inorganic particles. Meanwhile, the size of nanocomposite particles can be adjusted by varying the surfactant concentration and shear intensity during the miniemulsification. Therefore, miniemulsion polymerization is a powerful tool in preparing nanocomposite particles. To incorporate inorganic particles into the latex particles, many approaches were used to make inorganic particles well dispersed in the monomer phase. Erdem et al. [26–28] dispersed hydrophilic TiO_2 in the styrene monomer by using OLOA 370 (polybutene–succinimide pentamine) stabilizer, and obtained poly(styrene)/TiO_2 nanocomposite particles with an 80% TiO_2 encapsulation efficiency. Bechthold et al. [29] treated hydrophilic $CaCO_3$ particle surface with oleic acid prior to dispersing them into the oil phase, and obtained completely encapsulated $CaCO_3$/polystyrene nanocomposite particles via miniemulsion polymerization. Hoffmann et al. [30] encapsulated magnetic nanoparticles using oleoyl sarcosine acid or oleic acid as the first surfactant to disperse the magnetic particles into the styrene phase.

The aim of this research was to gain a fundamental understanding of the miniemulsion polymerization system, in which inorganic nanoparticles were much smaller than monomer droplets so that each monomer droplet contained many inorganic nanoparticles. Acrylate monomers containing the well-dispersed silica particles with the size of about 15 nm were miniemulsified after the coupling treatment of silica with 3-(trimethoxysilyl)propyl methacrylate, and are subsequently polymerized to obtain acrylate polymer/silica nanocomposite particles. The encapsulation efficiency of silica particles, the size distribution, morphology, and grafting of polymer onto silica of the nanocomposite particles were investigated.

2. Experimental

2.1. Materials

Commercially available methyl methacrylate/silica and butyl acrylate/silica dispersions with 20 wt% silica were supplied by Yuda Chemical Co., Ltd, Zhejiang, China. Two dispersions were mixed and diluted by pure methyl methacrylate (MMA) or butyl acrylate (BA) to form a series of acrylate/silica dispersions with a fixed MMA/BA weight ratio (3/1) and various silica weight fractions. MMA and BA monomers (Dongfang Chemical Co., Beijing) were distilled under reduced pressure and then kept refrigerated until use. 3-(Trimethoxysilyl)propyl methacrylate (MPS) coupling agent was obtained from Acros Organics Co., 2,2′azobisisobutyronitrile (AIBN), sodium dodecyl sulfate (SDS), hexadecane (HD), acetone, and tetrahydrofuran (THF) with analytical purity, were purchased from Shanghai No. 2 Chemistry Reagent Co., Ltd, Shanghai, China. Hydrofluoride acid was supplied by Juhua Group Co., Zhejiang, China.

2.2. Preparation of acrylate polymer/silica nanocomposite particles

A certain amount of MPS coupling agent was added into the acrylate/silica dispersion. After the mixture was magnetically agitated for 24 h at 40 °C under a N_2 atmosphere, certain amounts of HD, AIBN, and aqueous SDS solution were slowly added to the mixture. Then, the system was stirred and ultrasonicated for 60 s (output power 300 W, work time 10 s, pause time 5 s) under cooling with ice water to obtain a stable miniemulsion. Finally, the miniemulsion was added into a 200 ml jacket glass reactor fitted with a condenser, a N_2 inlet, a thermometer, and a paddle-type agitator. The miniemulsion polymerization was conducted at 60 °C for 5 h under a N_2 atmosphere. The recipes for the preparation of acrylate polymer and acrylate polymer/silica nanocomposite particles are shown in Table 1.

2.3. Characterization

2.3.1. Grafting of MPS and acrylate polymer onto silica

MPS modified acrylate/silica dispersions were vacuum dried at 50 °C for 12 h and extracted with acetone for 24 h to remove the residual acrylate and free MPS.

The weight fraction of carbon and hydrogen elements in the dried extraction residual was determined on a Flash EA1112 type Elemental Analyzer (ThermoFinnigan Co., Italy). The amount of MPS grafted onto the silica surface was calculated according to the Berendsen equation [34]. The grafting

Table 1
Recipes of miniemulsion polymerizations

Components (g)	1	2	3	4	5	6	7
Silica	0	4.1	0.4	1.0	2.0	4.0	4.0
BA	5.0	4.0	4.9	4.75	4.5	4.0	4.0
MMA	15	12	14.7	14.25	13.5	12	12
MPS	–	–	0.04	0.1	0.2	0.4	0.8
Deionized water	80.0	80.0	80.0	80.0	80.0	80.0	80.0
HD	0.68	0.68	0.68	0.68	0.68	0.68	0.68
SDS	0.289	0.287	0.288	0.287	0.290	0.288	0.288
AIBN	0.20	0.20	0.20	0.20	0.20	0.20	0.20

efficiency of MPS was defined as the weight percentage of the grafted MPS to the total MPS added for the modification.

Using the same method, the amount of acrylate polymer grafted on the silica in the acrylate polymer/silica nanocomposite particles was determined. The grafting degree of acrylate polymer was defined as the weight percentage of the grafted acrylate polymer to silica in the composite particles.

2.3.2. Viscosities of acrylate and acrylate/silica dispersions

The viscosities of acrylate and acrylate/silica dispersions were measured on a VT550 Rheometer (Haake Co., German) at 60 °C.

2.3.3. Size distributions of silica particles, miniemulsion droplets and latex particles

The size distributions of silica particles, the miniemulsion droplets and the latex particles were determined by dynamic light scattering (DLS) on a Zetasizer 3000 HS particle size analyzer (Malvern Instruments, USA). Soon after the sonication, the obtained miniemulsions were diluted with a saturated aqueous solution of acrylate monomers and SDS, and the measurement of size distribution was carried out immediately.

2.3.4. Encapsulation of silica in miniemulsion droplets and latex particles

The encapsulation efficiency of silica particles in the miniemulsion droplets was defined as the weight percentage of silica particles remaining in the droplets to the total silica added. The miniemulsion was centrifuged at 12,000 rpm for 60 min and the monomer phase was separated completely from water phase. The weight of the residual silica particles in the water phase was determined gravimetrically.

A known amount of the composite latex was centrifuged at 12,000 rpm for 60 min to form the serum and the deposit. The deposit was dispersed into water by magnetic stirring after the separation of the serum. The dispersion was centrifuged and the serum was separated again. This elution process was repeated several times to achieve the complete separation of the silica particles remaining in water phase (free silica particles) from the composite latex particles. The weight of silica in all collected serum was determined, and the weight percents of free silica particles and silica particles encapsulated by acrylate polymer could be calculated.

A known amount of the composite latex was slowly added to an excess HF solution. The resulted dispersion was dried and the weight of the residual silica was determined gravimetrically.

2.3.5. Morphology of silica particles, latex particles, and acrylate polymer/silica nanocomposite

The morphology of silica particles and the composite latex particles was directly observed by using a TEM-1230EX type transmission electron microscope (TEM) (JEOL Co., Japan).

The dried acrylate polymer/silica nanocomposite particles were melt-pressed at 170 °C and 30 MPa to form molded samples. TEM images were taken from microtomed ultrathin sections of the molded nanocomposites using the same device.

3. Results and discussion

3.1. Encapsulation efficiency of silica particles

The acrylate/silica dispersions used in the preparation of acrylate polymer/silica nanocomposites were transparent with no sediments. A typical TEM micrograph of silica particles collected from the acrylate dispersion is shown in Fig. 1. Silica particles are spherical and most of them were dispersed in the primary particle form with a diameter of about 15 nm. Fig. 2 shows the size distribution of silica particles in the acrylate medium. Most silica particles are smaller that 25 nm. The volume (weight) fraction of silica particles with the diameter greater than 25 nm was less than 4.0%.

Firstly, the original acrylate/silica dispersion was directly used to form a miniemulsion (Run 2 in Table 1). Fig. 3 shows the droplet size distribution of the resulted miniemulsion.

Two peaks appear in the distribution curve and the mean size of silica particles of the small peak is about 20 nm, which

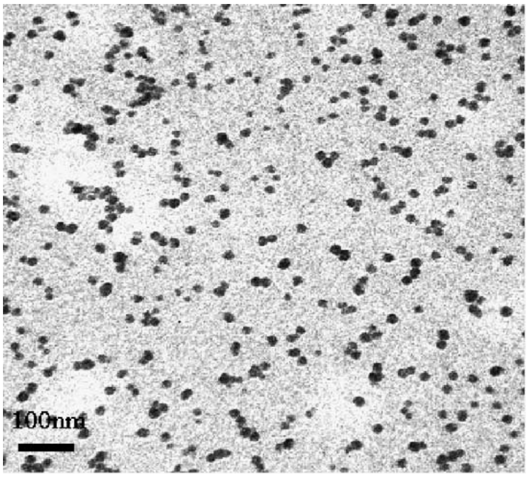


Fig. 1. TEM micrograph of silica particles.

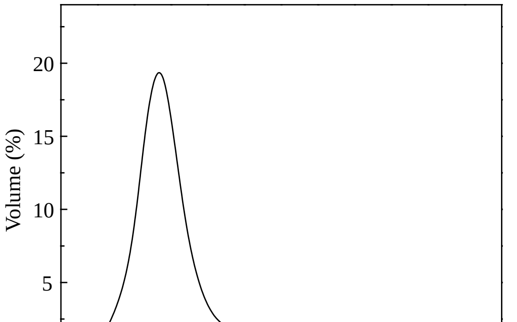


Fig. 2. Volume size distribution of silica particles dispersed in acrylate.

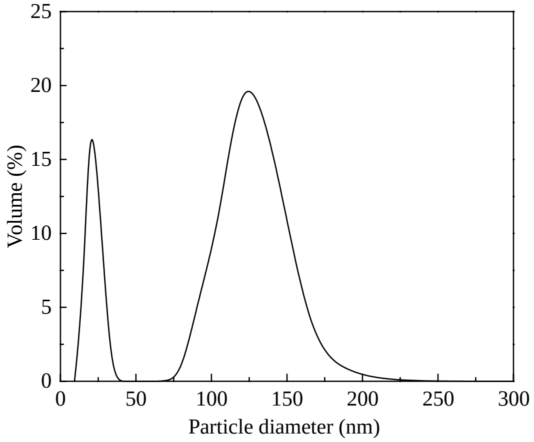


Fig. 3. Droplet size distribution of miniemulsion prepared by using the original acrylate/silica dispersion.

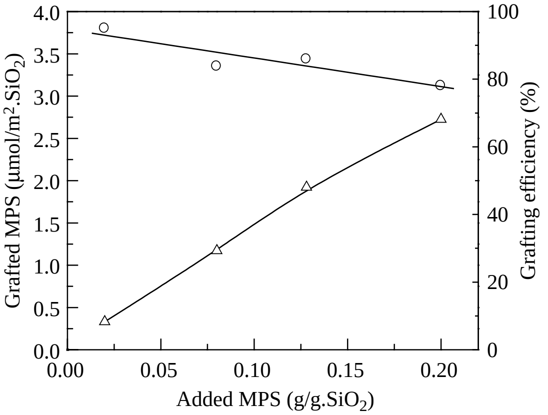
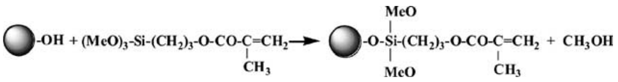


Fig. 4. Variations of grafted amount (△) and grafting efficiency (○) of MPS on silica surface with amount of MPS added.

is close to the size of silica particles in the original dispersion. The determined encapsulation efficiency of silica particles in the miniemulsion droplets is only 23.6%, which indicates that most silica particles migrated from the acrylate phase to the aqueous phase during the miniemulsification process, although silica particles can form a stable dispersion in the acrylate phase before the miniemulsification. This further illustrates that silica particles still exhibit strong hydrophilicity, and it is necessary to change the surface properties of the silica particles to ensure their encapsulation and well dispersion in the acrylate droplets after the miniemulsification.

MPS is regarded as a suitable coupling agent for the silica particles since trimethoxylsilyl groups can be hydrolyzed and be condensed with the silanol groups at the surface of silica particles and the alkylate chain of MPS is hydrophobic. The coupling reaction of MPS from silica particles surface is shown as follows:



$$\text{-OH} + (\text{MeO})_3\text{-Si-}(\text{CH}_2)_3\text{-O-CO-}\underset{\text{CH}_3}{\text{C}}\text{=CH}_2 \rightarrow \text{-O-}\overset{\text{MeO}}{\underset{\text{MeO}}{\text{Si}}}\text{-}(\text{CH}_2)_3\text{-O-CO-}\underset{\text{CH}_3}{\text{C}}\text{=CH}_2 + \text{CH}_3\text{OH}$$

The acrylate/silica dispersion with 20 wt% silica was modified with MPS. The effect of the amount of MPS added on both the grafted amount and grafting efficiency of MPS on silica surface is shown in Fig. 4. With the increase of the amount of MPS added, the amount of MPS grafted increases, while the grafting efficiency of MPS decreases.

The acrylate/silica dispersions modified with different amounts of MPS were miniemulsified. The effect of the amount of added MPS on the encapsulation efficiency of silica particles in the miniemulsion droplets is shown in Fig. 5.

It can be seen that the encapsulation efficiency of silica particles in the droplets increases with the increase of the amount of MPS added when the amount of MPS added is less than 0.08 g/g silica, and it levels off at 95% when the amount of MPS added is greater than 0.08 g/g silica. As shown in Table 1, 0.1 g MPS/g silica (Runs 3–6) and 0.2 g MPS/g silica (Run 7) were used for the modification of silica particles when the acrylate/silica dispersions were used in miniemulsion polymerizations, which would ensure the high encapsulation efficiency of silica particles in the minemulsion droplets.

After the miniemulsion polymerization, silica particles were distributed as the free silica in the aqueous phase, silica particles attached to acrylate phase at the water/-organic interface (incompletely encapsulated silica particles) and as silica/composites in the bulk of the organic phase (completely encapsulated silica particles). The free silica particles can be separated from the composite latex by the centrifugation and elution process, and the incompletely encapsulated silica particles and the completely encapsulated silica particles can be distinguished by the HF etching method.

The trial experiments were conducted to add HF solution to bare silica particles, acrylate polymer latex and the polymer latex/silica mixture. It was found that all bare silica particles were consumed, confirming the following reaction between silica and HF.

$$SiO_2 + 4HF = SiF_4\uparrow + 2H_2O$$

Whereas, the weight of acrylate polymer latex particles kept constant after the HF etching, and the polymer latex/silica

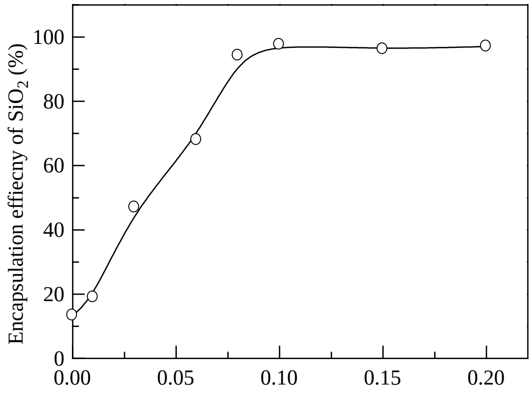


Fig. 5. Effect of the added MPS amount on the encapsulation efficiency of silica particles in the miniemulsion droplets.

Table 2
Weight percents of free, incompletely encapsulated and completely encapsulated silica in composite latexes

	Weight percent of free silica (%)	Weight percent of incompletely encapsulated silica (%)	Weight percent of completely encapsulated silica (%)
No. 2 latex	77.9	15.6	6.5
No. 6 latex	1.4	8.8	89.8

mixture only lost the weight of silica after the HF etching. So, it is considered that silica particles can be etched when they are exposed to HF, and the complete encapsulation of silica particles by polymer layer can prevent silica particles from being etched by HF.

The acrylate polymer/silica composite latexes prepared by using unmodified silica (No. 2 in Table 1) and by using MPS modified silica (No. 6 in Table 1) were slowly added into excess HF solutions, respectively. The weight percent of residue (completely encapsulated) silica after evaporation was measured gravimetrically. Combining the elution and etching results, the weight percents of the free silica, incompletely encapsulated silica and completely encapsulated silica were determined and are compared in Table 2 for the two formulations.

It can be seen that more than 75 wt% silica particles exist in the aqueous phase when the unmodified silica is used in the miniemulsion polymerization, whereas 98.6 wt% silica particles are combined with polymer and most of them are completely encapsulated by polymer when the modified silica is used in the miniemulsion polymerization. The encapsulation efficiency of silica particles in the composite latex particles was close to that in the corresponding miniemulsion droplets, indicating that silica particles would not migrated from the droplets during the miniemulsion polymerization process. So, the stable dispersion of silica particles in the miniemulsion droplets is the key step in preparing the polymer/silica nanocomposite with a high encapsulation efficiency of silica particles.

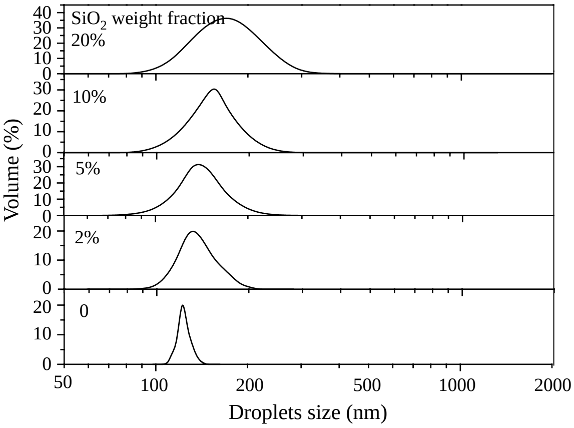


Fig. 6. Influence of silica weight fraction on the droplet size distribution of miniemulsions.

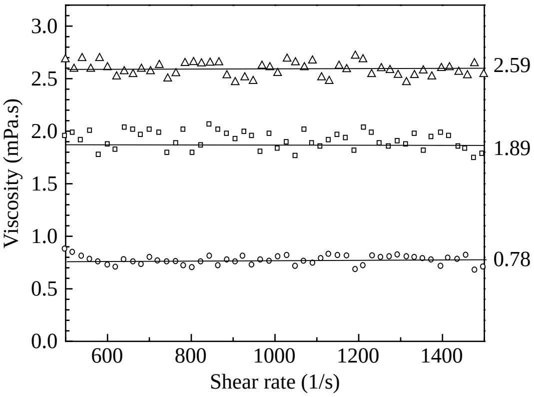


Fig. 7. Viscosities of acrylate monomers (○), acrylate containing 10 wt% silica (□) and 20 wt% silica (△) at various shear rates.

3.2. Size distributions of miniemulsion droplets and latex particles

The MPS modified silica/acrylate dispersions with the different silica weight fractions were agitated and ultrasonicated to obtain the miniemulsions. Fig. 6 shows the droplet size distributions of miniemulsions containing the different weight fractions of silica.

It can be seen that the average droplet size increases and the size distribution broadens as the weight fraction of silica increases. The introduction of nanometer-sized silica particles would change the physical properties of dispersion. Fig. 7 shows the viscosities of acrylate and acrylate/silica dispersions at different shear rates. It can be seen that the viscosity increases as more silica dispersed in acrylate phase. As a result, the acrylate phase became more difficult to be dispersed to small droplets during the miniemulsification process. On the other hand, the rigid silica particles would absorb more ultrasonic energy than acrylate monomers, which would cause the decrease of the effective ultrasonic power acted on the formation of droplets.

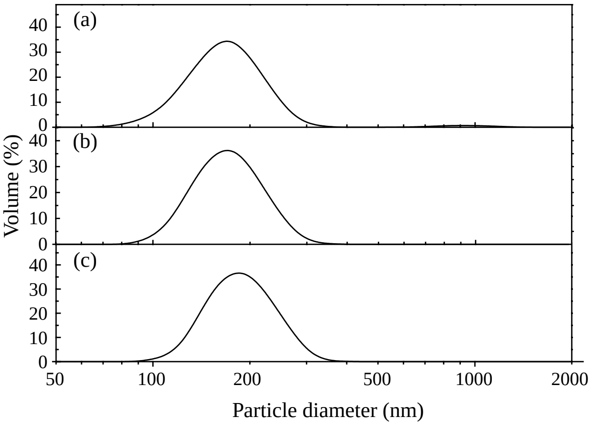


Fig. 8. Comparison on the size distribution of miniemulsion droplets and corresponding latex (Run 6, (a) before polymerization, (b) after polymerization, (c) stored for 6 months at room temperature).

Table 3
Monomers conversion, silica weight fraction in composite latexes

Run number	1	2	3	4	5	6	7
Monomers conversion (%)	89.4	85.5	87.2	84.8	83.4	80.7	80.5
Silica weight percent in composite (%)	0	23.1	2.3	5.8	11.8	23.7	23.8

The miniemulsions containing different weight fractions of silica were polymerized to form latexes. The size distribution of the latex particles is compared with that of the corresponding miniemulsion in Fig. 8. It shows that the size distribution of miniemulsion droplets and the corresponding latex are almost the same, even after the latex has been stored for 6 months at room temperature. This means that latex particles can copy 1:1 directly from droplets and the existence of silica has no obvious influence on the stability of latex.

3.3. Morphology of acrylate polymer/silica nanocomposite particles

The conversion of monomers to polymer and the weight fraction of silica in the composite latex (based on polymer weight) for Nos. 1–7 Runs in Table 1 are listed in Table 3. It can be seen that the conversion gradually decreases as the weight percent of silica increases.

Typical TEM micrographs of acrylate polymer particles (Run 1) and acrylate polymer/silica composite particles

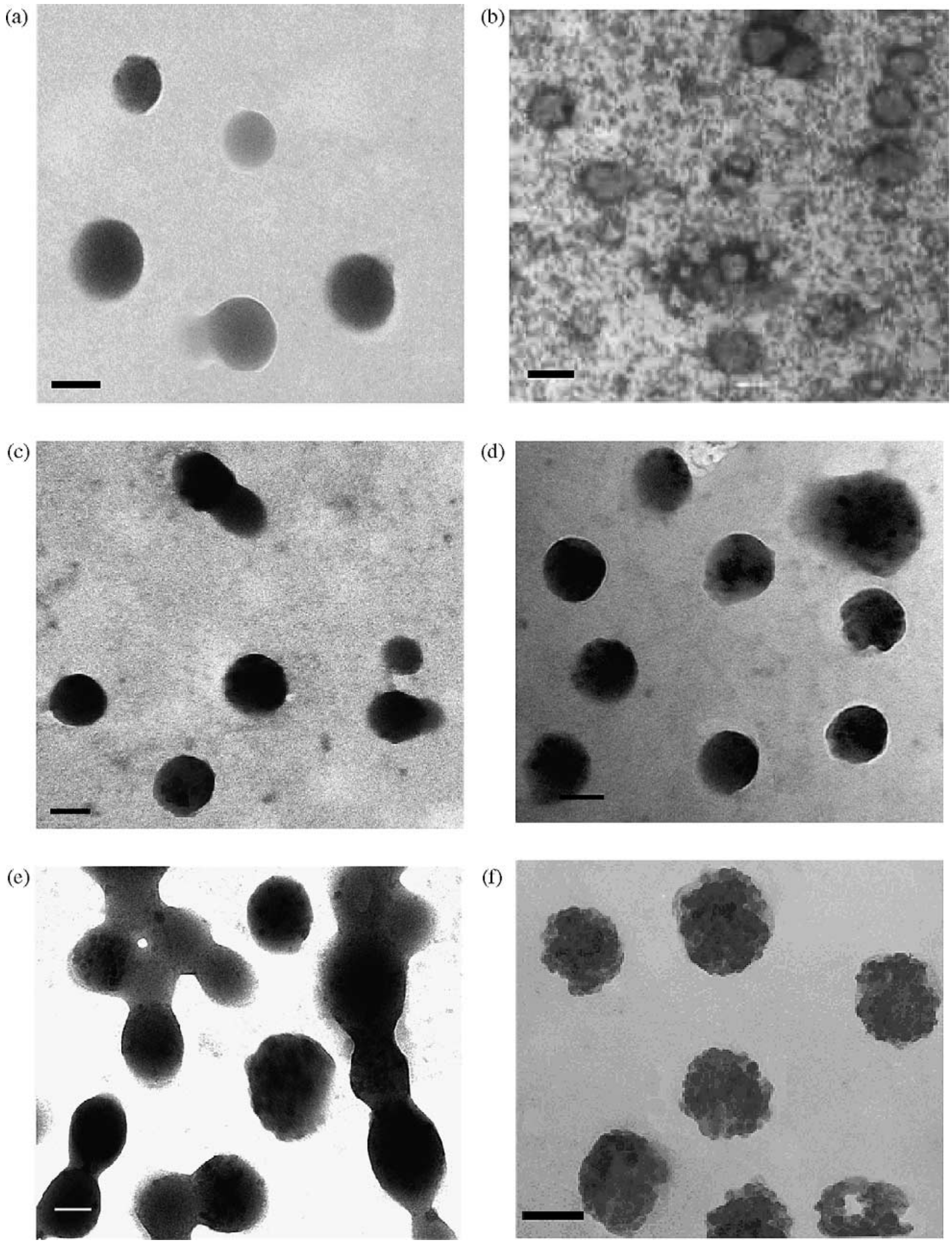


Fig. 9. Typical TEM micrographs of acrylate polymer particles (a), acrylate polymer/silica composite particles prepared by using unmodified silica (b) and by using MPS modified silica with different silica contents (c, 2.3%; d, 5.8%; e, 11.8%; f, 23.7%) (scale bar = 100 nm).

Table 4
Grafting degree of acrylate polymer and dispersion state of composite particles in THF solvent

Run number	2	3	4	5	6	7
Grafting degree (%)	2.5	62.2	64.8	58.1	59.7	204.8
State of dispersion	No sediment Transparent	No sediment Transparent	No sediment Transparent	No sediment Transparent	No sediment Transparent	Existing swollen particles

prepared by using unmodified silica/acrylate dispersion (Run 2) and by using MPS modified silica/acrylate dispersions (Runs 3–6) are shown in Fig. 9.

From the TEM micrograph of acrylate polymer/silica composite latex prepared by using the unmodified silica, it can be seen that most of silica particles escape from the oil phase and disperse in the continuous phase as so-called free silica particles. Whereas, the composite latex particles prepared by using modified silica have a ‘guava-like’ morphology with silica particles being encapsulated in the composite particles. Furthermore, there are no free silica particles found outside the polymer particles. The above result is consisted with the result listed in Table 2, and further confirms that almost all silica particles can be encapsulated by polymer when MPS modified silica is used in the miniemulsion polymerization.

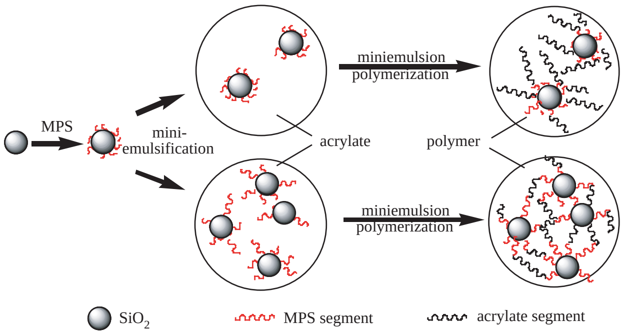


Fig. 10. Formation of grafted and crosslinked polymer chains in miniemulsion polymerization of acrylate monomers in the presence of MPS modified silica particles.

It can also be seen that the content of encapsulated silica particles increases as the weight fraction of silica increases. Especially, the composite particles were crammed with many silica particles when the weight fraction of silica was 23.7 wt%. Assuming that all silica and latex particles are spherical, and all silica particles have been evenly encapsulated in all composite particles, the average number of silica particles in each composite latex particle ([N]) can be calculated as follow

$$[N] = \frac{N_s}{N_c} = \frac{V_s/V'_s}{V_c/V'_c} = \frac{M_s\rho_c R_c^3}{M_c\rho_s R_s^3}$$

where N_s, V_s, V'_s, M_s, ρ_s and R_s represent the number, total volume, particle volume, mass, density, and radius of silica particles, and N_c, V_c, V'_c, M_c, ρ_c, and R_c represent the number, total volume, particle volume, mass, density, and radius of composite particles, respectively. Remembering that $M_s/M_c = 0.237$, $\rho_s = 2.6$, and $\rho_c = 1.17$, and assuming that $R_s = 15$ nm and $R_c = 160$ nm, the calculated average number of silica particles in each composite latex is 130.

3.4. Grafting of acrylate polymer onto silica

During the minemulsion polymerization of acrylate monomers in the presence of MPS modified silica particles, the grafting of acrylate polymer onto silica would be achieved through the copolymerization of acrylate monomers with the grafted MPS. The degree of grafting of acrylate polymer onto silica was determined for different nanocomposite particles and is listed in Table 4.

It can be seen that the degree of grafting of polymer onto silica in the composite particles increases as MPS modified silica used in the miniemulsion polymerization. When the same usage of MPS (0.10 g MPS/g silica) was applied for the modification of silica (Runs 3–6), silica in the composite particles exhibited almost the same degree of grafting of polymer as the weight percent of silica in the composite particles varied. As more MPS (0.20 g MPS/g silica in Run 7) used to modify silica, the grafting degree of polymer obviously increased.

The acrylate polymer/silica composite particles were dispersed in THF for 7 days, and the status of the resultant dispersions is described in Table 4. It can be seen that the

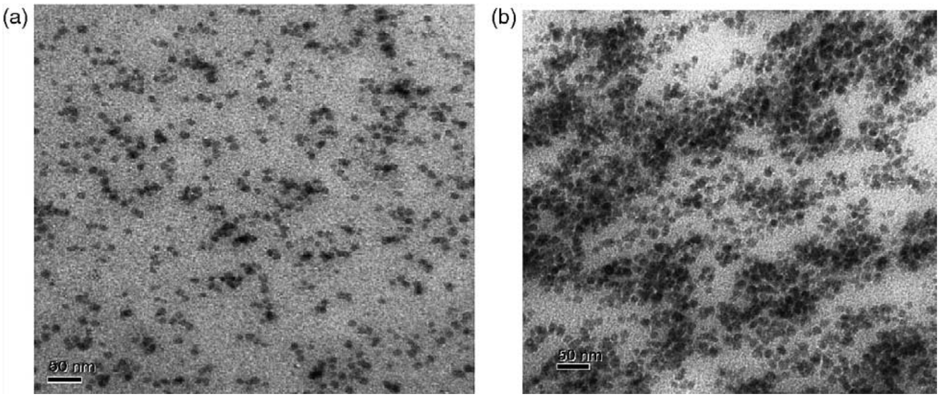


Fig. 11. TEM micrographs of acrylate polymer/silica nanocomposites (a, 2.4 wt% silica; b, 11.8 wt% silica).

transparent dispersions with no sediment were formed for Nos. 2–6 composite particles, indicating that the silica particles with grafted polymer can be stable dispersed in the solvent in the small size. In this case, the grafted polymer chains would provide the colloidal protection to silica particles. For the composite particles prepared in Run 7, the swelling of the solvent in the composite particles was appeared, indicating the formation of a crosslinked polymer network in the composite particles. The silica particles with grafted MPS exhibited many allyl groups and acted as a crosslinking agent in the copolymerization. When the concentration of allyl groups exceeded a critical value as the weight fraction of silica and the average number of grafted MPS molecules per silica particle increased, a crosslinked polymer network would be formed, in which the silica particles acted as the ‘crosslinking sites’. The formation of grafted and crosslinked polymer chains is represented in Fig. 10.

The grafted polymer chains would increase the dispersing degree of silica particles in the polymer matrix, and help to form a good interfacial adhesion between silica particles and polymer. Fig. 11 shows the typical TEM micrographs of the melt-processed acrylate polymer/silica nanocomposites containing 2.3 and 11.8 wt% silica. As expected, a well dispersion of silica particles in the polymer without serious aggregation was achieved.

4. Conclusions

It is convenient to synthesize acrylate polymer/silica nanocomposite particles through miniemulsion polymerization using the acrylate monomers/silica dispersion. The grafting of MPS onto silica particles is an effective way of improving the encapsulation efficiency of silica particles in the miniemulsion droplets and in the resultant composite latex particles. The existence of modified silica particles in the organic phase resulted in the formation of latex particles with greater average size and broadened size distribution. The acrylate polymer/silica nanocomposite latex particles prepared by using MPS modified silica exhibited a ‘guava-like’ morphology with some silica particles inlayed at the surface of latex particles.

Although the grafting of MPS onto the silica surface favors the grafting of polymer onto silica, chemically crosslinked polymer can be formed in the composite particles when the concentration of the grafted MPS was high. The silica particles in the composite particles exhibited a good dispersion ability in the solvent for polymer and in the polymer matrix. By varying the composition of feeding monomers, acrylate polymer/silica nanocomposite latex particles suitable for coatings or impact modifier for plastics can be obtained. The properties of the coating film and modified plastics can be improved due to the good dispersion of nano-sized silica particles and good interfacial adhesion between silica particles and the polymers.

Acknowledgements

Financial support from Science and Technology Department of Zhejiang Province, China, is appreciated.

References

[1] Kaempfer D, Thomann R, Mülhaupt R. Polymer 2002;43:2909.
[2] Fröhlich J, Niedermeier W, Luginsland HD. Composites 2005;A36:449.
[3] Odegard GM, Clancy TC, Gates TS. Polymer 2005;46:553.
[4] Ragostaa G, Abbatea M, Mustoa P, Scarinzia G, Mascia L. Polymer 2005;46:10506.
[5] Zheng K, Chen L, Li Y, Cui P. Polym Eng Sci 2004;44:1077.
[6] Caseri W. Macromol Rapid Commun 2000;21:705–22.
[7] Wang YW, Yen CT, Chen WC. Polymer 2005;46:6959.
[8] Hu GJ, Zhao CG, Zhang SM, Yang MS, Wang ZG. Polymer 2006;47:480.
[9] Caruso F, Spasova M, Susha A, Giersig M, Caruso RA. Chem Mater 2001;13:109.
[10] Xiong MN, Wu LM, Zhou SX, You B. Polym Int 2002;51:693.
[11] Xie XL, Liu QX, Li RKY, Zhou XP, Zhang QX, Yu ZZ, Mai YW. Polymer 2004;45:6665.
[12] Bourgeat-Lami E, Lang J. J Colloid Interface Sci 1998;197:293.
[13] Bourgeat-Lami E, Lang J. J Colloid Interface Sci 1999;210:281.
[14] Barthet C, Hickey AJ, Cairns DB, Armes SP. Adv Mater 1999;11:408.
[15] Furusawa K, Kimura Y, Tagawa Y. J Colloid Interface Sci 1986;109:69.
[16] Hergeth W, Starre P, Schmutzler K, Wartewig S. Polymer 1988;29:1323.
[17] Caris CHM, van Elven LPM, van Herk AM, German A. Br Polym J 1989;21:133.
[18] Espiard Ph, Guyot A. Polymer 1995;36:4391.
[19] Quaroni L, Chumanov G. J Am Chem Soc 1999;121:10642.
[20] Zhang K, Chen HT, Chen X, Chen ZM, Cui ZC, Yang B. Macromol Mater Eng 2003;288:380.
[21] Mizetani T, Arai K, Miyamoto M, Kimura Y. J Appl Polym Sci 2006;99:659.
[22] Luna-Xavier JL, Bourgeat-Lami E, Guyot A. Colloid Polym Sci 2001;279:947.
[23] Luna-Xavier JL, Guyot A, Bourgeat-Lami E. J Colloid Interface Sci 2002;250:82.
[24] Qi DM, Bao YZ, Huang ZM, Weng ZX. J Appl Polym Sci 2006;99:3425.
[25] Reculusa S, Mingotaud C, Bourgeat-Lami E, Duguet E, Ravaine S. Nano Lett 2004;4:1677.
[26] Erdem B, Sudol ED, Dimonie VL, El-Aasser MS. J Polym Sci, Polym Chem 2000;38:4419.
[27] Erdem B, Sudol ED, Dimonie VL, El-Aasser MS. J Polym Sci, Polym Chem 2000;38:4431.
[28] Erdem B, Sudol ED, Dimonie VL, El-Aasser MS. J Polym Sci, Polym Chem 2000;38:4441.
[29] Bechthold N, Tiarks F, Willert M, Landfester K, Antonietti M. Macromol Symp 2000;151:549.
[30] Hoffmann D, Landfester K, Antonietti M. Magnetohydrodynamics 2001;37:217.
[31] Tiarks F, Landfester K, Antonietti M. Langmuir 2001;17:5775.
[32] Zhang M, Gao G, Li C, Liu F. Langmuir 2004;20:1420.
[33] Zhang SW, Zhou SX, Weng YM, Wu LM. Langmuir 2005;21:2124.
[34] Berendsen GE, de Galan L. J Liq Chromatogr 1978;1:1561.