

Preparation of Polymer/Inorganic Nanoparticles Composites Through Ultrasonic Irradiation

QI WANG, HESHENG XIA, CHUHONG ZHANG

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

Received 15 April 2000; accepted 5 July 2000

ABSTRACT: In this paper, ultrasonic induced encapsulating emulsion polymerization was first used to prepare the novel polymer/inorganic nanoparticles composites. The behaviors of several inorganic nanoparticles (SiO_2 , Al_2O_3 , TiO_2) under ultrasonic irradiation, such as dispersion, crushing, and activation, were studied. The dispersion stability, morphology, and structure of the ultrasonic irradiated nanoparticles were characterized by means of transmission electron microscopy (TEM), Fourier transform infrared (FTIR), and spectrophotometry, respectively. The results show that the inorganic nanoparticles in the aqueous solution can redisperse more effectively by ultrasonic irradiation than by conventional stirring. This is the basis for preparation of polymer/inorganic nanoparticles composites. By this technique, the long-term stable latex, which mainly consists of polymer/inorganic nanoparticles composite latex particles, were successfully prepared. TEM, FTIR, thermogravimetric analysis, X-ray photoelectron spectroscopy, spectrophotometry, and element analysis confirmed that well-dispersed nanoparticles were encapsulated by the formed polymer, and the thickness of encapsulating polymer layer was in the range of 5–65 nm. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1478–1488, 2001

Key words: polymer/inorganic nanoparticles composites; ultrasonic irradiation; stability

INTRODUCTION

Polymer/inorganic nanoparticle composites have attracted more and more attentions recently. They combine the advantages of polymers, e.g., elasticity, transparency, or dielectric properties, and inorganic nanoparticles, e.g., specific absorption of light, magnetoresistance effects, chemical activity, and catalysis. However, it is very difficult for inorganic nanoparticles to disperse in the

polymer matrix at the nano scale through conventional mixing, because nanoparticles have very high surface energy and will agglomerate during mixing. Generally, many approaches have been tried to solve the problem: e.g.

1. The vapor deposition technique¹: the metal vapor deposits on the surface of the polymer matrix to form the nano-sized metal particles.
2. Precursor technique²: the precursors of inorganic particles are introduced in the polymer matrix, then through appropriate chemical reactions to produce metal nanoparticles or semiconductor nanoparticles.
3. Nanoreactor technique³: the precursors of nanoparticles are introduced into the

Correspondence to: Qi Wang.

Contract grant sponsor: National Science Foundation of China; contract grant number: 29974020.

Contract grant sponsor: Ministry of Education of China.

Journal of Applied Polymer Science, Vol. 80, 1478–1488 (2001)
© 2001 John Wiley & Sons, Inc.

“nanoreactor,” which consists of the micelle resulted from the amphilic block or graft polymer, and nanoparticles forms in situ through appropriate chemical reactions, such as reduction.

4. Intercalation polymerization⁴: monomer, initiator, and layer inorganic materials such as clay are mixed together and polymerized. (The layer inorganic materials disperse at the thickness of nano scale in the polymer matrix.)
5. Supramolecular self-assembly technique⁵: by complicated self-assembly process, the nanometer supramolecular structure with fiber, layer, or tubal can be produced.
6. Encapsulating polymerization⁶: under the proper condition, the polymerization of monomer occurs on the surface of nanoparticles, forming polymer layer encapsulating particles.

Among other things, encapsulating polymerization may be the most attractive strategy to prepare polymer/inorganic nanocomposites, because the type of nanoparticles and encapsulating polymer can be varied in a wide range to meet the requirement. However, the challenges for encapsulating polymerization areas are that (1) nanoparticles should be redispersed at the nano scale in reaction medium during polymerization and (2) polymerization of monomer should occur on the surface of nanoparticles. Therefore, the development of nanocomposites demands new techniques to realize dispersion, stabilization, and composting of inorganic nanoparticles in polymer matrix.

Ultrasonic irradiation, as a new technology, has been widely used in chemical reactions. When ultrasonic waves pass through a liquid medium, a large number of microbubbles form, grow, and collapse in very short time, about a few microseconds, which is called ultrasonic cavitation. Sonochemical theory calculation and the corresponding experiments⁷ suggested that ultrasonic cavitation can generate local temperature as high as 5000 K, and local pressure as high as 500 atm, heating and cooling rate greater than 10^9 K/s, a very rigorous environment. Therefore, ultrasound has been extensively applied in dispersion, crushing, and activation of particles, as well as initiation of polymerization.

In the present study, the ultrasonic irradiation technique was first employed to prepare polymer/inorganic nanoparticle composites. By taking advantages of the multieffect of ultrasound, i.e., dis-

persion, crushing, activation, and initiation, the polymerization of monomer on the surface of nanoparticles could be realized while the inorganic nanoparticles disperse in the liquid medium at nano scale, so as to get the composites containing stable nanoparticles encapsulated by polymer.

As the first paper of a systematic study, we report here the preparation of polymer/inorganic nanoparticles composites through ultrasonic irradiation. The behaviors of several inorganic nanoparticles (SiO_2 , Al_2O_3 , TiO_2) under ultrasonic irradiation, such as dispersion, crushing, and activation were studied. The morphology, structure, and dispersion stability of the ultrasonic irradiated nanoparticles were characterized by means of transmission electron microscopy (TEM) and Fourier transform infrared (FTIR), and the novel polymer/inorganic nanoparticles composites prepared through ultrasonic irradiation were investigated by TEM, FTIR, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and element analysis.

EXPERIMENTAL

Materials

Nanoparticles: SiO_2 , 10–15 nm, Al_2O_3 , 17 nm, TiO_2 , 27 nm, Zhoushan Nanomaterial Limited Company, Zhejiang, China.

n-Butyl acrylate (BA): CP, Tianjin Chemical Reagent Factory, was washed three times with 10% aqueous solution of sodium hydroxide and distilled water to remove the inhibitor hydroquinone, dried with anhydrous sodium sulfate, then vacuum distilled.

Cetyl trimethylammonium bromide (CTAB): AR, Beijing Chemical Reagent Company, China.

Sodium lauryl sulfonate (SLS): CP, Shanghai Xiangde Chemical Factory, China.

Apparatus

The equipment employed in this research was 20 kHz ultrasonic generator, Fisher Sonic Dismembrator Model 550 (Fisher Scientific Co.) or VC-1500 (Sonic & Materials) (Fig. 1), with the following characters:

- Standard titanium horn of diameter 13 mm, replaceable flat stainless steel tip.
- Self-designed and made in-house vessels.

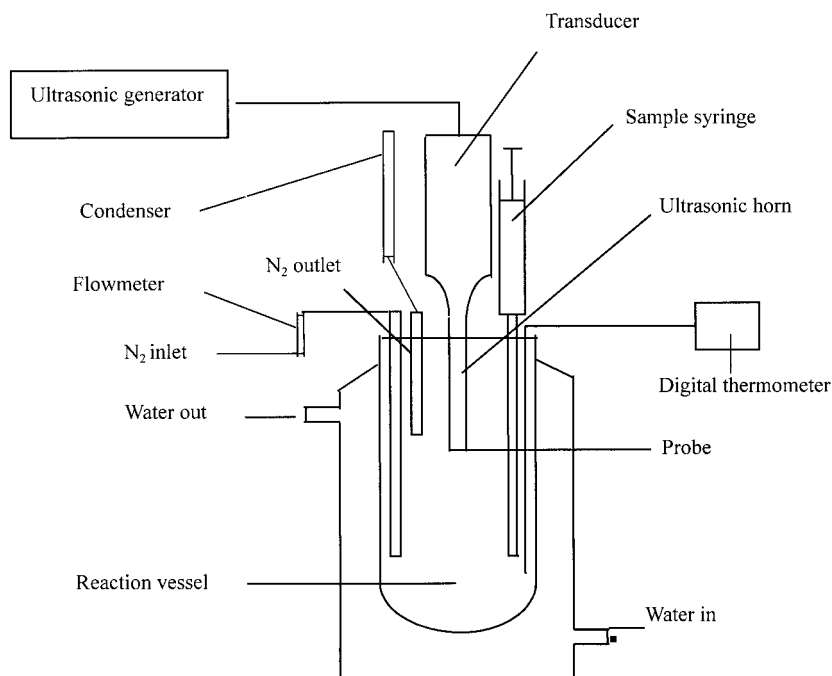


Figure 1 Schematic diagram of the ultrasonic induced encapsulation emulsion polymerization.

- Adjustable power out.
- Constant medium temperature by circulating thermostated water.
- Measurable reaction temperature by digital thermometer.
- Measurable N_2 gas purging rate by gas flowing meter.
- Condenser to reduce the monomer vaporization.

Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly in the mixture emulsion system. During the polymerization thermostated water was circulated to maintain the temperature constant, and N_2 purging rate keeps constant.

Preparation of Polymer/Inorganic Nanocomposite Through Ultrasonic Irradiation

Specific amounts of purified monomer, surfactant aqueous solution, and nanoparticles were introduced into the reaction vessel, deoxygenated by bubbling with oxygen-free nitrogen for 2 min in the reaction vessel, and water was circulated to maintain a certain temperature. Then the ultrasound generator was switched on and the emul-

sion was subjected to ultrasonic irradiation. After a certain reaction time, ultrasonic irradiation was stopped. Half of the prepared polymer emulsion was stored for dispersion stabilization observation, the rest was poured into ice-cold methanol to coagulate and deemulsify, then the precipitated material was filtered, washed, dried under vacuum, and weighed to ascertain the conversion gravimetrically in the usual way.

Characterization

Particle size and particle size distribution were determined by TEM performed on JEM 100-CX instrument. The particles include nanoparticles and composite latex particles. The latex particles were analyzed after dyeing, and the nanoparticles in the composite latex were analyzed directly without dyeing.

IR analysis of the samples were performed on a Nicolet 560 FTIR spectrometer.

TGA analysis of the samples was performed on TA2000 instrument.

To obtain the content of the emulsifier adsorbed on the surface of nanoparticles, The C, O and N contents of the nanoparticles were determined by element analysis with a Italy Carlo Erba 1106 Element Analysis Instrument

The Si content of the samples was determined by XPS performed on a NP-1 XPS instrument. The measurement was carried out at 15 kV of power and 9 mA of electrical current by employing fixed transmission energy.

The dispersion stability of nanoparticles in the aqueous solution was characterized with a 721 Spectrophotometer.

The charge property of nanoparticles was determined by electrophoretic analysis with a DYY-III-4 Electrophoresis Apparatus.

RESULTS AND DISCUSSION

Behaviors of Nanoparticles Under Ultrasonic Irradiation

This study focused on the preparation of polymer/inorganic nanoparticles composites through ultrasonic irradiation by taking its advantages of multieffect, i.e., dispersion, crushing, and activation. First, the behaviors of nanoparticles under ultrasonic irradiation was investigated.

Dispersion of Nanoparticles Under Ultrasonic Irradiation

After conventional stirring or ultrasonic irradiation for 10 min, the variation of absorbance of nano SiO₂, nano Al₂O₃, and nano TiO₂ in water or 2% SLS aqueous solution with the time are shown in Figures 2, 3, and 4, respectively.

From Figures 2–4 we can see that the absorbance of all the systems decreases with the time. However, the absorbance of the ultrasonic irradiated systems decreases more slowly than that of the conventionally stirred systems. Also, the final absorbance of the former systems is higher than that of the latter systems.

It is difficult to characterize on-line the dispersion of nanoparticles in the aqueous solution during ultrasonic irradiation and conventional stirring. The variation of absorbance with the time may reflect indirectly the level of dispersion. The nanoparticles are easy to agglomerate due to the high surface energy, and the agglomerated particles will precipitate, leading to a decrease in concentration of particles in the liquid phase. Thus, the absorbance of the liquid will decrease with the time. Ultrasonic cavitation has very strong mixing and dispersion effect, much stronger than conventional stirring; in fact, ultrasound has a molecular stirring effect. Therefore, nanoparticles

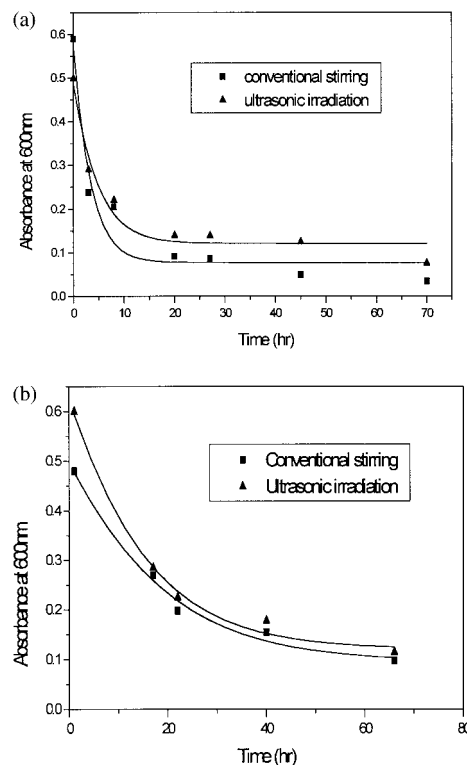


Figure 2 Absorbance–time curves of SiO₂ nanoparticles in (a) water and (b) 2% SLS aqueous solution after conventional stirring or ultrasonic irradiation for 10 min.

are well dispersed in the aqueous solution after ultrasonic irradiation, responsible for the low rate of agglomeration and precipitation. Figure 5 compares the size of nano silica in 0.05% NaOH and 0.5% CTAB aqueous solution after conventional stirring and ultrasonic irradiation. The size of ultrasonic irradiated nanoparticles is 40–60 nm, much smaller than that of conventionally stirred nanoparticles, and dispersed much better also.

It is obvious that ultrasound has much better dispersion effect on particles than the conventional stirring, and nanoparticles can be dispersed at the nanometer level in the aqueous solution through ultrasonic irradiation. This provides the basis for the preparation of polymer/inorganic nanoparticles composites.

Besides, from Figure 5(b), the irregular surfaces of nanoparticles produced after ultrasonic irradiation can be observed. This suggests that ultrasound has the crushing effect on the solid particles. The strong shock wave and the high rate stream (about 400 km/s) produced from ultrasonic cavitation should be responsible for this observation.

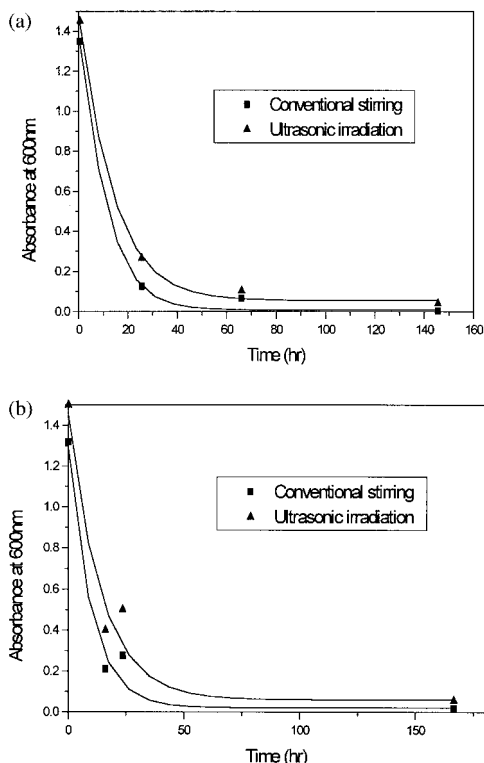


Figure 3 Absorbance–time curves of Al_2O_3 nanoparticles in (a) water and (b) 2% SLS aqueous solution, after conventional stirring or ultrasonic irradiation for 10 min.

Activation of Nanoparticles Under Ultrasonic Irradiation

The activation behavior of nanoparticles in the aqueous solution under ultrasonic irradiation was studied. Nano SiO_2 particles (surface modified with 2,2-methylchlorosilicane) in anionic surfactant (SLS) and cationic surfactant (CTAB) aqueous solution were irradiated under ultrasound, then were washed by centrifuging for 15 times (2 min every time), and dried under vacuum. The obtained product was characterized by FTIR. As shown in Figure 6, the characteristic peaks of the modifying agent 2,2-methylchlorosilicane at 2981, 1384, and 879 cm^{-1} become weaker or even disappear, suggesting that ultrasound has “cleaning” effect on nanoparticles, creating fresh surfaces with much higher activity. This will benefit the later polymerization of monomers on the nanoparticle surfaces. There have been some other reports on the clearing and activation effect of ultrasonic irradiation.⁷

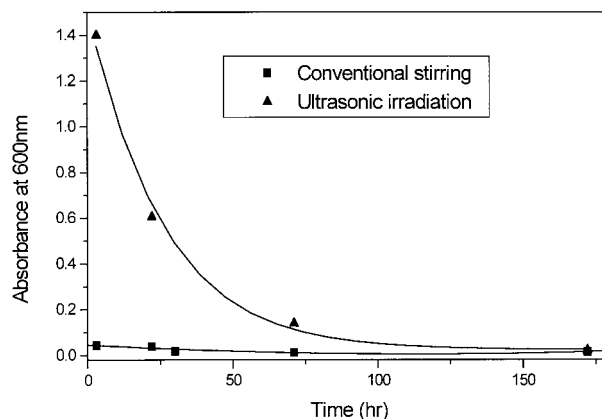


Figure 4 Absorbance–time curves of TiO_2 nanoparticles in water after conventional stirring or ultrasonic irradiation for 10 min.

It can be concluded that ultrasonic irradiation can realize the dispersion, crushing, and activation of nanoparticles in liquid medium. This pro-

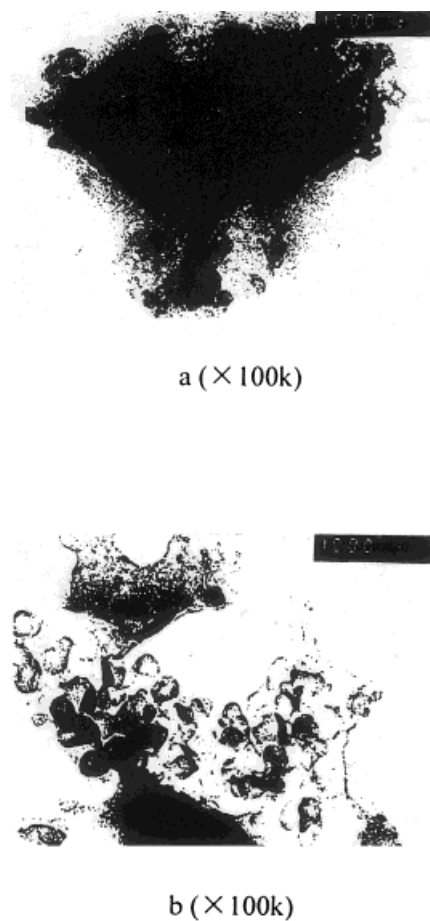


Figure 5 TEM micrograph of nano silica in 0.05% NaOH and 0.5% CTAB aqueous solution 1 h after (a) conventional stirring and (b) ultrasonic irradiation.

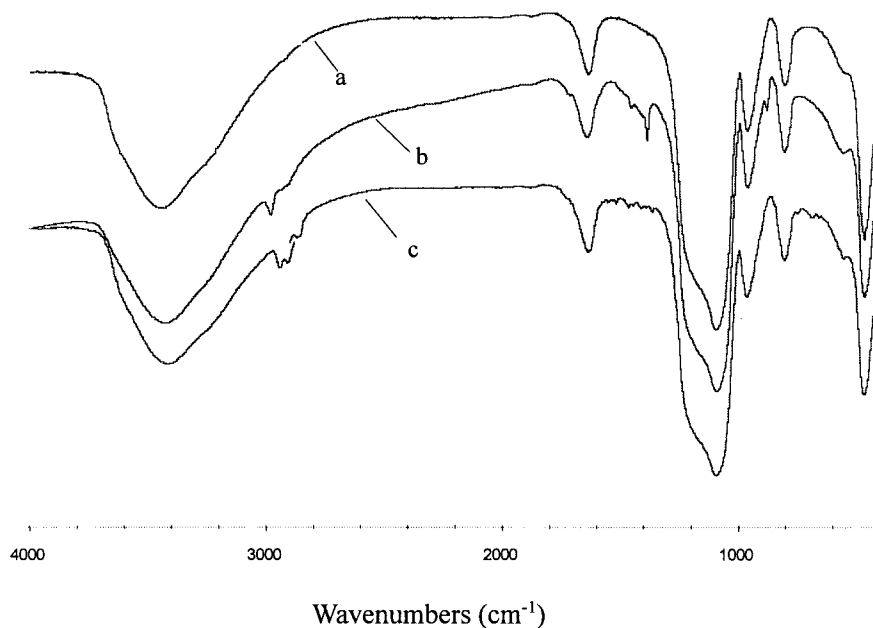


Figure 6 FTIR spectra of various hydrophobic, nano silica, absorbing emulsifiers: (a) SLS, (b) pure nano silica, and (c) CTAB.

vides the basis for the encapsulating polymerization of monomer on the surface of dispersed nanoparticles.

Ultrasonic Induced Emulsion Polymerization

The premise condition for ultrasonic induced encapsulating emulsion polymerization of monomers is that ultrasound can initiate polymerization of monomers without any chemical initiator. We have reported the successful ultrasonic induced emulsion polymerization of BA and methyl methacrylate (MMA).^{8,9} Figure 7 shows the time-conversion curves for the two monomers. It can be seen, under ultrasonic irradiation, the conversion of BA amounts to 91% in 11 min and the conversion of MMA amounts to 65% in 30 min, which is a very encouraging result offering a basis for preparation of polymer/inorganic nanoparticle composites.

Ultrasonic Induced Polymerization of Monomers on Nanoparticle Surfaces

By taking advantages of the multieffect of ultrasonic irradiation, i.e., dispersion, crushing, and activation on the nanoparticles as well as initiation of polymerization of monomers, the polymer-

ization of monomers on the surface of nanoparticles that are dispersed at nano scale can be realized, and a novel polymer/inorganic nanoparticle composite can be prepared. We conducted the ultrasonic induced encapsulating emulsion polymerization of monomer BA in the presence of hydrophobic porous nano silica and hydrophilic spherical nano silica without any added initiator. The long-term stable polymer/inorganic nanoparticles composite latex can be obtained by this

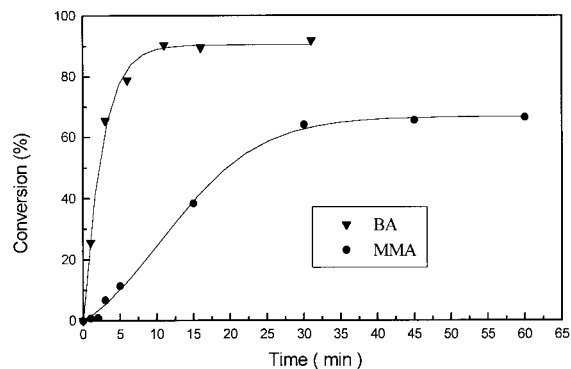


Figure 7 The time-conversion curves of ultrasonic induced emulsion polymerization of monomer MMA and BA.

method. The reason for such successful preparation was proposed. Since the size of nanoparticles is very small and the specific surface area is so large, under appropriate operating conditions, a large amount of cationic surfactant can strongly be adsorbed on the surface of nanoparticles with negative charge. The adsorbed surfactant molecules are considered to form a local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and an upper layer of head groups in contact with solution, which is called admicelles.⁸ When surfactant molecules are adsorbed on the surface of nanoparticles, the surface of nanoparticles becomes hydrophobic, which favors the adsorption of hydrophobic monomer such as BA. At the same time, the presence of admicelles promotes the adsorption of the monomer in the admicelles, and helps to prevent the formation of general micelles formed by self-aggregation of surfactant molecule. Those formed admicelles can capture the radicals produced by ultrasonic cavitation, to *in situ* initiate the encapsulating emulsion polymerization of monomer on the surface of nanoparticles in the admicelles. Once the reaction has started, additional monomer from the bulk solution diffuses into the admicelles.¹⁰ By adjusting the operating conditions, the polymerization in the admicelles can occur, and the competitive polymerization in the bulk solution can be minimized. Besides, the intense shock wave and stream resulted from ultrasonic cavitation can produce active sites on the surface of nanoparticles to initiate the polymerization of monomer on the surface of nanoparticles. At the same time, surfactant, water, monomer, and the formed polymer on the surface of nanoparticles can be decomposed to produce radicals and *in situ* initiate the polymerization of monomer. The prepared latex can be treated by coagulation, washing and drying to obtain the polymer/inorganic nanoparticles composite.

The formation and structure of poly(*n*-butyl acrylate) (PBA)/nano silica composites obtained through ultrasonic irradiation were identified and analyzed by means of TEM, FTIR, TGA, extraction, etc.

TEM Analysis

The latex particles in the composite latex prepared through ultrasonic irradiation were observed through TEM. The nano silica in the composite latex particles were analyzed without dy-

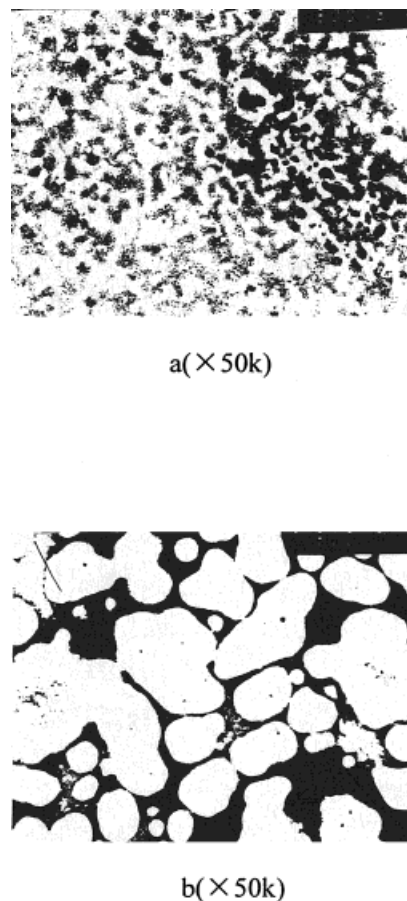


Figure 8 TEM micrograph of (a) nano silica and (b) composite latex particles (dyed with PTA). PBA latex contains well dispersed hydrophobic porous nano silica.

ing, while the composite latex particles were analyzed after dying with phosphorus tungsten acid (PTA).

TEM micrographs of the nanoparticles and the composite latex particles in PBA latex containing well-dispersed hydrophobic porous nano silica or hydrophilic spherical nano silica are shown in Figures 8 and 9, respectively. From Figures 8(a) and 9(a), it is clear that hydrophobic porous nano silica and hydrophilic spherical nano silica SiO_2 are dispersed at a nano scale level. The particle size of hydrophobic porous nano silica is in the range of 20–40 nm, and the particle size of hydrophilic spherical nano silica SiO_2 is in the range of 30–50 nm. From Figures 8(b) and 9(b), we can see that the size of the composite latex particles is in the range of 50–150 nm. Through attentive observation, we can see one or a few “black dot,” which represents nano SiO_2 particles in the com-

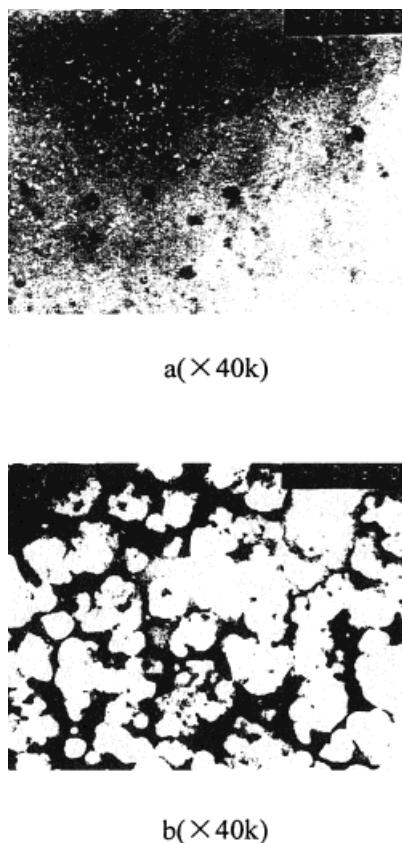


Figure 9 TEM micrographs of (a) nano silica and (b) composite latex particles (dyed with PTA). PBA latex contains well-dispersed hydrophilic spherical nano silica.

posite latex particles. The agglomerates of a few latex particles can be found in Figures 8(b) and 9(b). This is because, during the preparation of sample for TEM observation, the polymer PBA with low glass transition temperature (T_g) readily collapses and deforms. However, nanoparticles are isolated by the polymer layer encapsulating on the particles. TEM observations confirm that inorganic nanoparticles are isolated and encapsulated by PBA, and the thickness of the encapsulating polymer layer is in the range of 5–65 nm. All these encouraging results suggest that ultrasonic induced encapsulating emulsion polymerization is feasible to prepare polymer/inorganic nanocomposite.

FTIR Analysis

Figure 10 shows the IR spectra of the nano silica, PBA, and PBA/nano silica composite. The charac-

teristic peaks of PBA/nano silica composite are summarized in Table I.

As shown in Figure 10 and Table I, the characteristic peaks of PBA and nano silica can be found in the spectrum of PBA/nano silica composite. However, the wavenumbers of some peaks were shifted; for example, the peak at 3426 cm^{-1} attributed to the —OH of nano silica shifts to 3438 cm^{-1} , the peak at 1640 cm^{-1} attributed to the Si—O of nano silica shifts to 1633 cm^{-1} , the peak at 1460 cm^{-1} attributed to the —CH_2 of PBA shifts to 1455 cm^{-1} , the double peak at 1378 cm^{-1} and 1379 cm^{-1} attributed to the —CH_2 of PBA becomes single peak at 1386 cm^{-1} , and the peak at 1255 and 1168 cm^{-1} attributed to the C—O of PBA shifts to 1246 and 1166 cm^{-1} . Especially, the fingerprint region below 1000 cm^{-1} is very different from that of pure PBA and nano silica, indicating a different new structure.

To further confirm the nanostructure in the PBA/nano silica composite, we recorded IR spectra of PBA containing poor dispersed nano silica, which was prepared by mechanically mixing the pure PBA latex and the nano silica, and PBA containing well-dispersed nano silica, which was prepared through ultrasonic induced encapsulating emulsion polymerization. As shown in Figure 11, the two IR spectra are different. Most of characteristic peaks shift a few wavenumbers. Those shifts are summarized in Table II. Especially, the fingerprint region below 1000 cm^{-1} also has many significant differences. Clearly, the IR spectrum of PBA containing poor dispersed nano silica is similar to the superimposition of pure PBA and nano silica.

It is evident that the prepared PBA/nano SiO_2 composite is different from the simple mixture of pure PBA and nano silica. In combination with the TEM analysis, this further confirms the existence of nanoparticles encapsulated by polymer.

Table I Characteristic Peaks of PBA Containing Well-Dispersed Nano Silica

Wavenumbers (cm^{-1})	Attribution
3438	—OH
1735	C=O
1246	C—O—C
1165	C—O—C
1067	Si—O

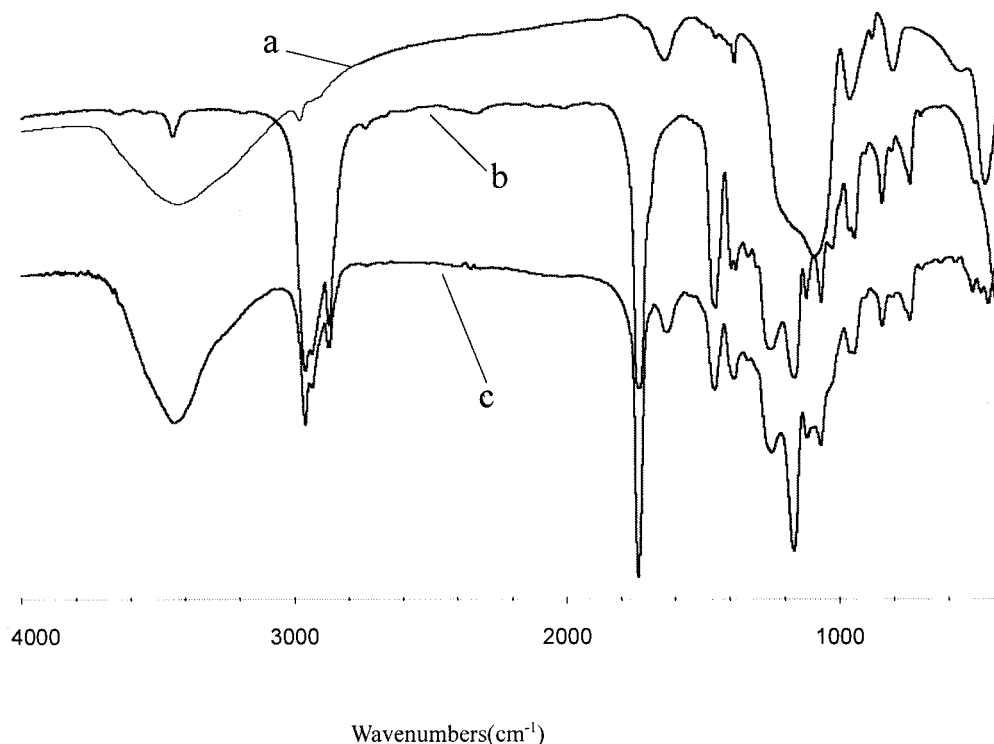


Figure 10 FTIR spectra of (a) pure SiO_2 , (b) pure PBA, and (c) PBA containing well-dispersed nano silica.

TGA Data

Figure 12 is the TGA curves of PBA containing well-dispersed nano silica or poor dispersed nano silica. And the data obtained by TG analysis are listed in Table III. From Figure 12 and Table III, it can be seen that the thermolysis temperature of PBA containing well-dispersed nano silica is higher than that of PBA containing poorly dispersed nano silica. This may be attributed to the structure of polymer encapsulating nanoparticles.

Dissolution and Extraction Experiment

To further confirm that the nano silica was dispersed at the nano level, we conducted the dissolution and extraction experiment for the obtained polymer/inorganic nanoparticle composites.

The 0.5 g PBA samples containing well-dispersed nano silica or poorly dispersed nano silica were dissolved in the acetone, respectively. We find that the solution of the former is almost transparent, the absorbance at 400 nm is 0.005, but the solution of the latter is turbid, the absorbance at 400 nm is 0.065, 13 times that of the former. This suggests that the dispersive size of

silica in the former is much smaller than that in the latter, i.e., ultrasonic induced encapsulating emulsion polymerization can realize the nano level dispersion of nano silica in PBA matrix.

The 1.98 g PBA containing well-dispersed nano silica prepared through ultrasonic induced encapsulating emulsion polymerization was wrapped with filter paper with a pore diameter of about 100 nm, then was extracted 48 h in solvent extractor with acetone. It is interesting to note that there is nothing remained on the dried filter paper, and the extracted acetone solution is almost transparent. The film made with the extracted acetone solution was examined by means of XPS. The Si atom was detected, and the ratio of the number of Si and O atom is 4.1: 95.8. The content of nano silica in the composite film so calculated is about 4.2 %, a little bit lower than the initially introduced content, probably due to the loss during transferring. Also, the extracted acetone solution was observed through TEM. As shown in Figure 13, the nano silica with a size of about 50 nm was aggregated together. So, the above experiments further confirm that the nano silica is dispersed

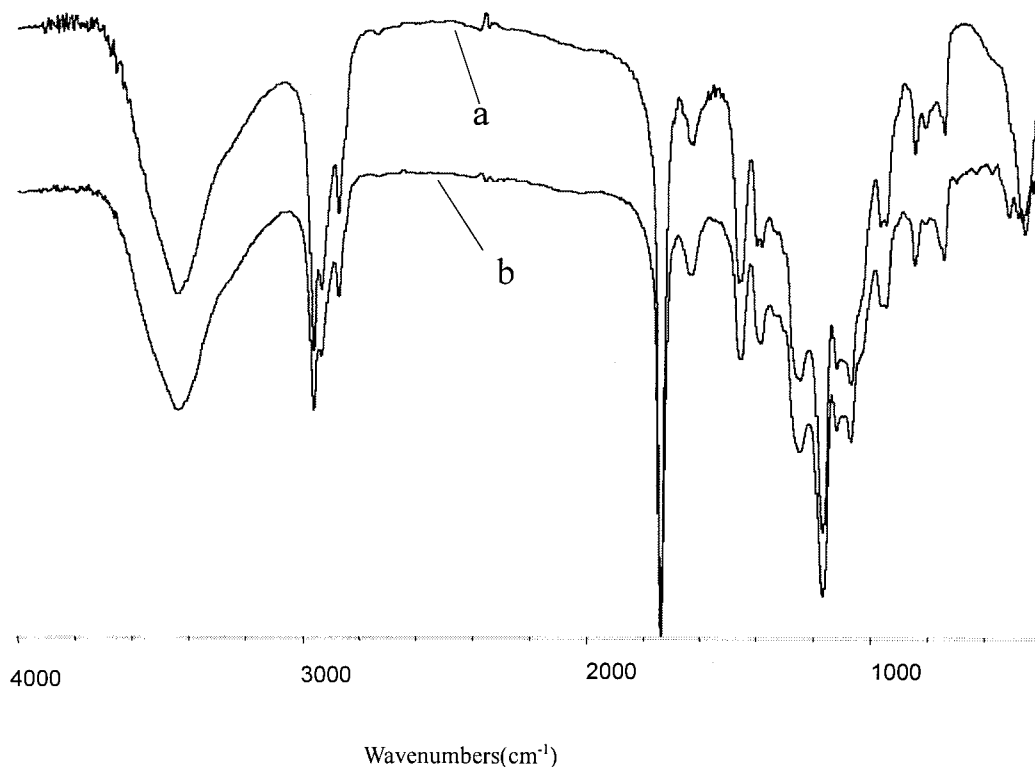


Figure 11 FTIR spectra of (a) PBA containing poorly dispersed nano silica and (b) PBA containing well-dispersed nano silica.

at the nano level in the PBA/nano silica composite prepared through ultrasonic irradiation.

CONCLUSION

- Spectrophotometry, FTIR, and TEM confirm that the inorganic nanoparticles in the aqueous solution can redisperse more effectively through ultrasonic irradiation than by conventional stirring, which was the basis for

monomers to polymerize on the surface of nanoparticles.

- Subjected to ultrasonic irradiation, BA and MMA monomers can be polymerized without any chemical initiator.
- By taking advantages of the multieffect of

Table II Characteristic Peaks of (a) PBA Containing Well-Dispersed Nano Silica; (b) PBA Containing Poor-Dispersed Nano Silica

Group	Wavenumbers (cm ⁻¹)	
	a	b
—OH	3438	3444
Si—O	1633	1625
—CH ₂ —	1456	1462
—CH ₃	1386	1380 (double)

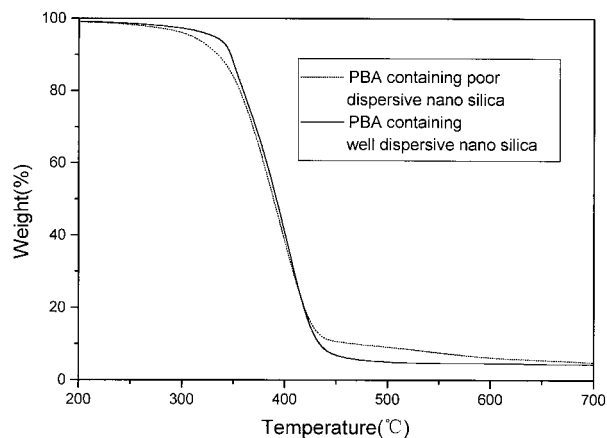


Figure 12 TGA curves of (a) PBA containing well-dispersed nano silica and (b) PBA containing poorly dispersed nano silica.

ultrasound, i.e., the dispersion, crushing, activation, and initiation, the long-term stable PBA latex that contains polymer encapsulating nano silica was prepared through ultrasonic induced encapsulating emulsion polymerization. Further processing of the composite latex leads to formation of PBA/nano silica composite.

- TEM, FTIR, TGA, dissolution, and extraction experiments confirm that nano silica was encapsulated by PBA, not being only the simple mixture of pure PBA and nano silica, and the nano silica dispersed in PBA matrix at a nano level.

Ultrasonic irradiation realizes the dispersion, stabilization and composting of nanoparticles in the polymer matrix, and offering a new way to deal with the challenges encountered in preparing polymer/inorganic nanocomposite materials.

This research is supported by National Science Foundation of China (29974020) and Ministry of Education of China.

Table III Results of TGA^a

	<i>a</i>	<i>b</i>
Ti (°C)	354	346
Tf (°C)	425	420

^a *a*: PBA containing well-dispersed nano silica; *b*: PBA containing poor-dispersed nano silica; Ti: the initial thermolysis temperature; Tf: the final thermolysis temperature.

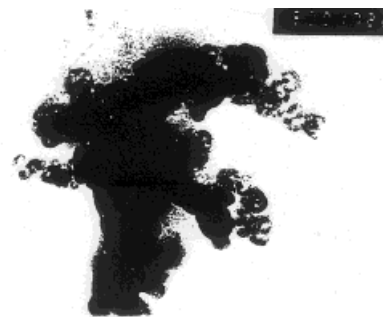


Figure 13 TEM micrograph of polymer encapsulating nano silica particles in the acetone solution after 48 h extraction ($\times 50$ k).

REFERENCES

1. Akamatsu, K.; Deki, S. *Nanostructured Materials* 1997, 8, 1121.
2. Watkins, J. J.; McCarthy, T. J. *Polym Mater Sci Eng* 1995, 73, 158.
3. Mayer, A.; Antonietti, M. *Colloid Polym Sci* 1998, 276, 769.
4. Qiao, F.; Li, Q.; Qi, Z.; et al. *Acta Polymer (China)* 1997, 3, 135.
5. Weller, H. *Adv Mater* 1993, 5(2), 193.
6. Bourgeat-Lami, E.; Espiard, Ph.; Guyot, A. *Polymer* 1995, 36(23), 4385.
7. Suslick, K. S. *Science* 1990, 3, 1439.
8. Wang, Q.; Xia, H.; Liao, Y.; Xu, X. Presented at The 6th Pacific Polymer Conference, Dec. 7–11, 1999, Guangzhou, China.
9. Liao, Y.; Wang, Q.; Xia, H.; Xu, X. Presented at The 6th Pacific Polymer Conference, Dec. 7–11, 1999, Guangzhou, China.
10. O'Haver, J. H.; Harwell, J. H.; et al. *Langmuir* 1994, 10, 2588.