Available online at: http://journal.ippi.ac.ir

Preparation and Characterization of TiO$_2$/Poly(St-*co*-MAA) Core/Shell Composite Particles

Jianmin Zhang[1,2], Jungang Gao[1*], Xiuguo Sun[2], Zheng Peng[2], and Jianzhi Diao[2]

(1) College of Chemistry and Environmental Science, Hebei University, Baoding-071002, P.R. China
(2) School of Material Science and Engineering, Shijiazhuang Railway Institute, Shijiazhuang-050043, P.R. China

A B S T R A C T

The TiO$_2$/poly(St-*co*-MAA) core/shell composite particles were prepared via emulsion polymerization. The cetyltrimethyl ammonium bromide (CTMAB) was used as surfactant of emulsion polymerization. The effect of the styrene/MAA weight ratio on the morphology of the composite particles was investigated. The inorganic/organic core/shell composite particles were characterized by Fourier transform infrared spectra (FTIR), translation electron microscope (TEM), thermogravimetric analysis (TGA) and particle size analyzer. The results of FTIR and TGA measurements showed that TiO$_2$ was successfully coated by poly(St-*co*-MAA). The particle size analysis and TEM result of the resulting composite particles indicated that these particles had a narrower size distribution and regularly spherical core/shell morphology. At the same time, there was one TiO$_2$ particle within each TiO$_2$/poly(St-*co*-MAA) composite particle and the average particle diameter of composite particles was 191 nm. In addition, the results showed that the conversion of monomers was 78.0% in this emulsion polymerization and copolymer of poly(St-*co*-MAA) constituted of 62.6% composite particles. The encapsulation was best when the styrene/MAA weight ratio was 3/2, and the encapsulation efficiency reached 85.8%.

(∗) To whom correspondence to be addressed.
E-mail: zhangjm@sjzri.edu.cn

INTRODUCTION

Composite particles consisting of an inorganic core and a polymer shell, due to the possibility of combining the advantages of different materials, have attracted much attention of material scientists and researchers. For instance, composite particles are designed to enhance the overall performance of composites in mechanical, electrical and photonics properties [1-3]. Besides, functional composite particles can be prepared from inorganic particles and a polymer containing functional groups such as carboxylic acid, hydroxyl, amine, and sulphate [4,5]. As a consequence of its encapsulation with

Archive of SID

Preparation and Characterization of TiO$_2$ ...   Zhang J. et al.

the polymer, particle surface would change, and its compatibility with other polymers and dispersion stability in the blending system can be improved [6]. In fact, this type of composite particles have received some interest in a wide range of industrial fields, such as adhesives, textiles, pesticides, drugs, diagnosis, toner and paint [7-11].

Although many methods exist, but the conventional emulsion polymerization is the most frequently used technique for the encapsulation of inorganic particles by polymer. Jose-Luiz et al. [12] used an emulsion polymerization approach along with a cationic initiator system to encapsulate silica particles modified with a non-ionic polyoxyethylenic surfactant. Dong-Guk et al. [13, 14] studied encapsulation of titania particles by dispersing them in water using emulsifiers (SLS and Triton X-100). Yu et al. [15] modified the surface of silica particles with hydroxy-propyl-methyl cellulose (HPMC) coupling agents in studies of their encapsulation by conventional emulsion polymerization. Viala et al. [16] tried to encapsulate inorganic pigments such as TiO$_2$ or Fe$_x$O$_y$ (black, yellow or red), using NP30 as surfactants. Choi et al. [17] investigated the encapsulation of cadmium sulphide particles with polyacrylonitrile by gamma-irradiation and emulsion polymerization. Tan et al. [18] studied the polymerization of methyl methacrylate on the surface of pigment particles by using soapless emulsion polymerization method. Alternative polymerization techniques, as suspension or dispersion, have also been employed to encapsulate inorganic particles. Duguet et al. [19] modified the surface of alumina through the condensation of 3-(trimethoxysilyl) propyl-methacrylate (gamma-MPS) in studies of their encapsulation by aqueous suspension polymerization. Dispersion polymerization was also employed for encapsulation of submicron size titania particles within different polymers such as poly[(St-*co*-DVB)-MAA] [20,21] and poly[(MMA-*co*-EGDMA)-MAA] [22].

In the present paper a rather simple encapsulation procedure of TiO$_2$ particles based on emulsion polymerization of styrene and MAA is described. The ability to carry out particle nucleation in emulsion droplets containing the inorganic particles plus the ability to nucleate all the droplets created are shown to lead to an efficient encapsulation of the inorganic par-

ticles. A good dispersion and dispersion stability of inorganic particles in the monomers medium requires the adsorption of a dispersing agent at the solid/monomers interface. The effect of the styrene/MAA weight ratio on the morphology of the composite particles are investigated. The composite particles are characterized by means of FTIR spectroscopy, transmission electron microscopy (TEM), thermogravimetric analyzer (TGA) and particle size analyzer. The aim of the study is to gain a better understanding of the fundamentals of emulsion polymerization applied to encapsulation of nano size inorganic particles, which is important from an academic as well as an industrial point of view.

EXPERIMENTAL

Materials
The recipe used in the preparation of TiO$_2$/poly(St-*co*-MAA) core/shell composite particles is shown in Table 1. The monomers, styrene (St) and methacrylic acid (MAA) were all analytically pure grade and were supplied by the Tianjin Chemical Reagent Co. (Tianjin, China). To remove inhibitor, the styrene was washed with a 5% sodium hydroxide solution followed by a deionized water washing. TiO$_2$ particles with average particle size close to 100 nm were used as core materials, which were produced according to literature [23]. Cetyltrimethyl ammonium bromide (CTMAB), ammonium persulphate (APS), NaHCO$_3$ and NaOH are all analytically pure and supplied by the Beijing Chemical Reagent Co. (Beijing, China).

Table 1. Recipes for encapsulation of TiO$_2$ by emulsion polymerization.

Symbol	No.1	No.2	No.3
TiO$_2$ (g)	2.0	2.0	2.0
CTMAB aqueous solution* (mL)	1.0	1.0	1.0
St (g)	4.0	3.3	3.0
MAA (g)	1.0	1.7	2.0
St/MAA(w/w)	4/1	2/1	3/2
APS (mg)	100	100	100
Deionized water (mL)	300	300	300

* concentration: 25 mg/mL.

Polymerization Procedure

2 Grams of TiO$_2$ powder, 1 mL CTMAB aqueous solution containing 25 mg of CTMAB and 300 mL of deionized water were poured into a 500 mL of four-necked flask. Then the whole system was agitated by ultrasonic cleaner (KQ-250DB, Kunshan, China) for about 30 min at room temperature. Following sonication of the particles, the flask was equipped with a mechanical stirrer, thermometer, reflux condenser, and a nitrogen gas inlet and outlet. Then the flask was immersed into a 70ºC water bath and the nitrogen gas was bubbled through the solution for deoxygenation. The stirring speed was fixed to 250 rpm. After 30 min, the mixture of the desired amount of monomers (Table 1) was poured into the reaction flask and stirred for 15 min. Then 0.10 g APS was added into reactor. The polymerization was carried out at 70ºC for 6 h and, by using a saturated sodium bicarbonate solution, the pH was held during the reaction process between 8 and 10. Then, the reaction product was poured into a saturated NaCl solution with the same volume before being stirred thoroughly. The latexes were separated from the slurry by vacuum filtration. The filter cake was washed with deionized water for five times and anhydrous ethanol, respectively. Finally, the particles were dried in a vacuum oven at room temperature for a period of 24 h and it was used to obtain the specimens to be morphologically characterized and to determine the particle size distribution.

Separation of Polymer Particles from Composite Particles

To determine the encapsulation efficiency (percentage of the total polymer that is present in the composite particles) and the percentage of polymer in the composite particles (P%), it was required to separate the polymer particles (particles without TiO$_2$) from the composite particles. Such separation process was carried out by centrifugation of the original latexes at 1.5×10^4 rpm for 15 min. The supernatant serum was removed, and the precipitate was dispersed again in water. The operation was reproduced until the serum was no longer turbid [10,24]. The polymer particles were separated from the supernatant serum by vacuum filtration. Finally, the bottom phase and the supernatant serum were separately dried in a vacuum oven at room temperature for a period of 24 h and they

were used to obtain the specimens to be characterized by means of FTIR and thermogravimetry. The encapsulation efficiency and the P% value can be calculated considering the polymer and composite particles weights.

The conversion of monomers (C%) was determined by means of conventional gravimetric method and was calculated using the following equation:

$$\text{Conversion (C\%)} = (M_0 - M_1) / M_2 \times 100\% \qquad (1)$$

where M_0 (g) was the mass of total resulting composite particles, M_1 (g) was the mass of charged TiO$_2$ particles, and M_2 (g) was the mass of charged monomers.

The percentage of P(St-*co*-MAA) in composite particles (P%) and encapsulation efficiency (E%) were calculated by the following equations:

$$P\% = M_5 / M_4 \times 100\% \qquad (2)$$

$$E\% = \frac{M_5}{M_7} \times 100\% = \frac{M_1 \times P\%}{(M_2 \times C\%)(1 - P\%)} \times 100\% \quad (3)$$

where M_5 (g) the mass of P(St-*co*-MAA) in composite particles, M_4 (g) the mass of composite particles, and M_7 (g) the total mass of copolymer [P(St-*co*-MAA) in composite particles and free copolymer] formed.

The theoretical percentage of copolymer in composite particles (T%) was calculated by the following equations:

$$T\% = M_2 / (M_1 + M_2) \times 100\% \qquad (4)$$

Characterization

The morphology of the composite particles was observed by transmission electron microscopy (TEM, Jeol-1200 EX II, Japan). The composite particles were dispersed in deionized water in an ultrasonic bath for 10-30 min and a drop of diluted dispersion was put on a carbon film supported by a copper grid using the accelerated voltage of 80 kV.

The IR spectra were recorded with a Fourier transform infrared spectrophotometer (FTIR, Nicolet Avatar 330, USA). The composite particle sample was ground with dried KBr powder, and compressed into a plate. The KBr plate was scanned by an FTIR

spectrophotometer.

The thermogravimetric analysis was determined by thermogravimetric analyzer (TGA/SDTA 851ᵉ, Mettler, Switzerland). About 3-4 mg of sample was put into an Au crucible for thermogravimetric analysis. The heating rate was 10℃ /min in an argon atmosphere. The recorded temperature range was from 50℃ to 650℃.

The particle size and its distribution were measured by zeta potential and particle size analyzer (Malvern Zetasize 3000 HSA, England). Before measurement, the samples were diluted with deionized water at 1:5000 volume ratio.

RESULTS AND DISCUSSION

Effect of the Weight Ratio of St/MAA on the Encapsulation

In conventional emulsion polymerization [10], the principal site of particle nucleation is either in the aqueous phase or in the swollen monomer micelles. In the presence of inorganic particles dispersed in the aqueous phase, an additional site can be the surface of the particles. However, the competition between these mechanisms can lead to both polymer particles containing no inorganic particles and unencapsulated particles, besides the encapsulated ones.

The TEM image of bare TiO₂ particles is shown in Figure 1a. Such particles exhibit an irregular shape (approximately spherical) with a very broad particle size distribution, with evidence of particle aggregation; the presence of numerous tiny particles can also be observed.

The TEM micrographs in Figures 1b-1d show TiO₂ particles covered with polymer. Figure 1b and Figure 1c show the images of the latexes prepared with the styrene/MAA weight ratio being 4/1 and 2/1. There is a rough surface due to the presence of small poly(St-*co*-MAA) cluster surrounding the inorganic seed particles. The particles are not perfectly spherical and their diameters are among a wide distribution and there are no TiO₂ cores noticed in some of the particles.
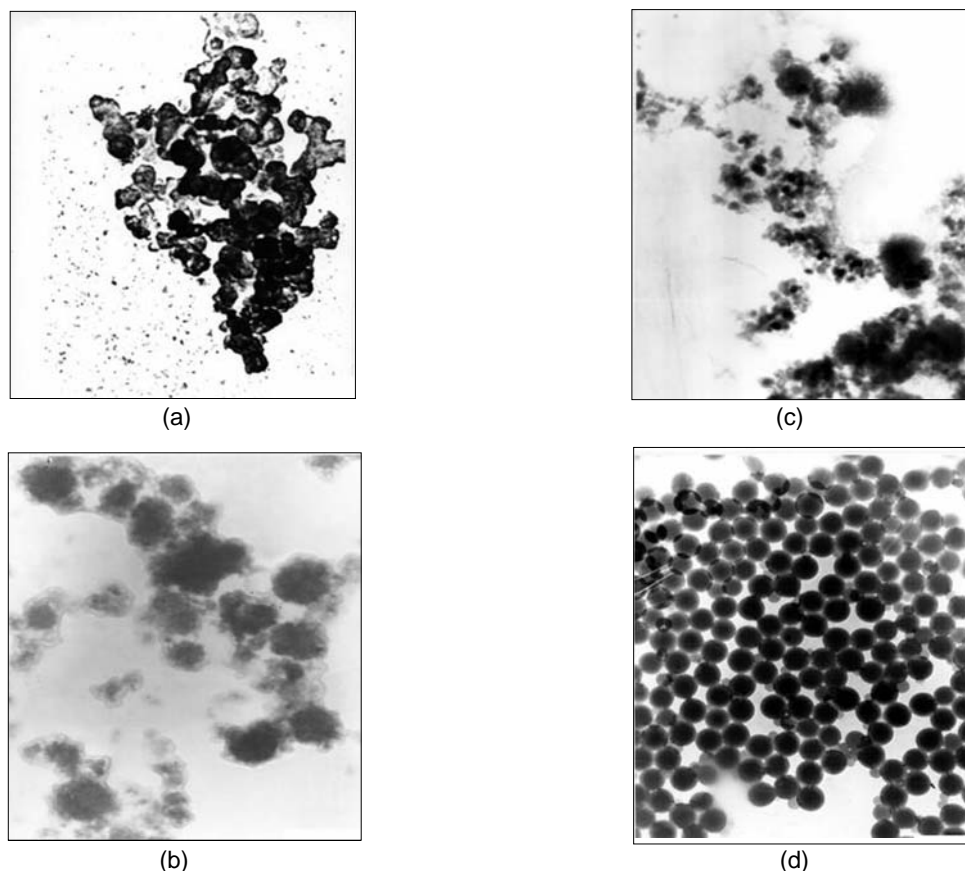
Figure 1d shows the TEM images of the latexes

Figure 1. TEM Micrographs for: (a) bare TiO₂, (b) latex No. 1, (c) latex No. 2, and (d) latex No. 3.

prepared with the styrene/MAA weight ratio being 3/2. The central black spot and translucent parts in the microspheres show TiO_2 particles and copolymer of P(St-*co*-MAA), respectively. It can be certain that the TiO_2 particles have been encapsulated into the copolymer phase. No noticeable amount of unencapsulated TiO_2 particles is observed on the particle surface. The microspheres reveal smooth surface and spherical shape and the particle diameters are reasonably uniform. It is also observed from the image that the dispersibility and dispersion stability of the composite particles are the best, and no coagulation has been observed during polymerization, ensuring a successful encapsulation of TiO_2 particles with the styrene/MAA weight ratio being 3/2. This resulted from the stronger polarity and solubility of the monomer MAA. The larger MAA content existing in monomers, the higher concentration of monomers was in aqueous phase, then more monomer molecules could diffuse to the surface of the TiO_2 particles. As a result, the speed of polymerization reaction on the particle surface would be faster. More close-grained and smooth composite particles can be obtained. Well encapsulated TiO_2 particles possess better dispersibility and dispersion stability [6,13]. So we believe that St/MAA copolymer shells covered the surfaces of TiO_2 particles and suppressed the aggregation of the composite particles effectively. However, there were also some polymer particles which contained no TiO_2 particles.

The particle size and size distribution of bare TiO_2 and the latex No.3 were determined by particle size analyzer, as shown in Table 2 and Figure 2. It was noticed that there were five columns in the particle size distribution of bare TiO_2 particles, which were located at about 70, 95, 102, 122, 145 nm, respectively (Figure 2a). The average particle diameter of bare TiO_2 was 104 nm and its standard deviation was 13.5. In the case of latex No.3, the average composite particle diameter was 191 nm and its standard deviation was 17.4 while the polymer particles which contained no TiO_2 particle had sizes around 95-105 nm (Figure 2b). The distribution columns were located at about 70, 90, 115, 150, 195 nm, respectively.

From TEM micrograph of bare TiO_2 particles (Figure 1a), we could find that there were many gaps and empty space around the particles. It was well known that such particles, owing to weak force that stack them together, could be easily separated in a solvent. During polymerization, St and MAA might have entered the gaps and empty space between the primary particles under a strong shear environment. Hence, polymerization could be initiated by diffusion of an initiator and the heat released inside the gaps would lead to breakdown of bare TiO_2 particle agglomerates [25]. The encapsulation efficiencies were dependent on the size and stability of the TiO_2 particles obtained in the initial dispersion. Smaller and more stable particles resulted in an improvement in the amount of encapsulating poly(St-*co*-MAA) [10]. The average size of composite particles increased with increasing the amount of poly(St-*co*-MAA) shell coated on the surface of TiO_2 particles. So we believe that poly(St-*co*-MAA) shells covered the surfaces of TiO_2 particles and suppressed the aggregation of TiO_2 particles effectively. By observing TEM micrograph of the latexes (Figure 1d), it is evident that the shape of the encapsulated particles

Table 2. Particle size and size distribution of bare TiO_2 and latex No. 3.

Symbol	Bare TiO₂		Latex No. 3	
	Particle size(nm)	Intensity (%)	Particle size(nm)	Intensity (%)
1	69.8±10	5.1	70.2±11	4.4
2	95.2±11	8.8	89.7±12	12.5
3	102.0±11	69.9	115.1±9	3.6
4	122.7±9	12.0	150.2±13	1.8
5	144.9±13	4.2	195.0±13	77.7

* Averages and errors based on three measurements on a given sample.
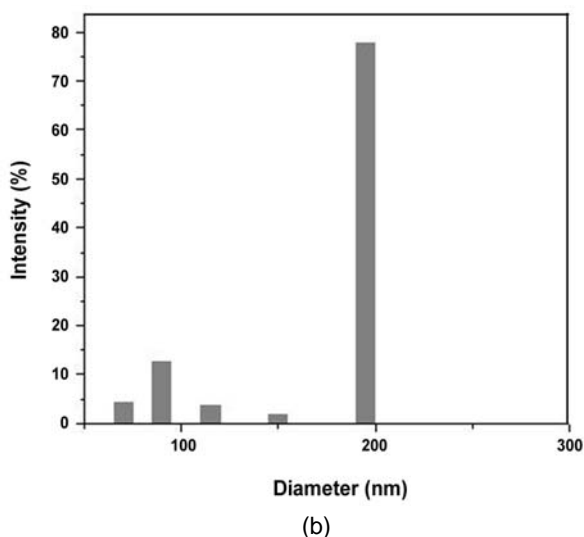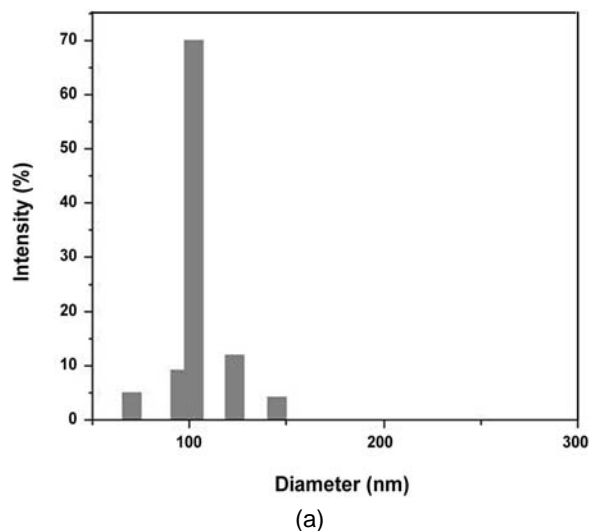
(a)

(b)

Figure 2. Particle size distribution for: (a) bare TiO₂, and (b) latex No. 3.

are spherical and smooth, and there was one TiO₂ particle within each TiO₂/poly(St-*co*-MAA) composite particle. The composite particle size was observed to be larger and its distribution tended to a single column around 195 nm.

FTIR Analysis
FTIR Spectroscopy results for the samples are shown in Figure 3. Figure 3a corresponds to the bare TiO₂, and Figure 3b and Figure 3c to the composite particles No.3 and polymer particles No.3, respectively. In Figure 3a, the vibration absorption at low frequencies, such as from 500 to 800 cm^{-1}, showed the existence of a Ti-O-Ti backbone. In the spectrum of Figure 3b and Figure 3c, absorption bands at 1000-2000 cm^{-1} and
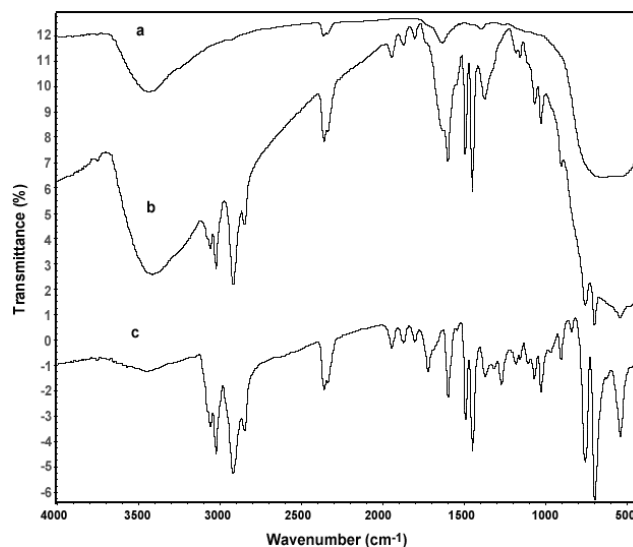

Figure 3. FTIR Spectra for: (a) bare TiO₂, (b) particles present in bottom phase of latex No. 3, and (c) polymer particles present in supernatant serum of latex No. 3.

around 3000 cm^{-1} were observed. It was possible to observe a broadband region of 3200-3600 cm^{-1} associated to the hydroxyl groups. The bands in the region 2800-3000 cm^{-1} correspond to the CH₂ and CH₃ groups of polymer backbone. The peak with wavenumber of 3025 cm^{-1} and 3060 cm^{-1} corresponding to the C-H stretching of benzene ring, and the weak peaks at 1944 and 1873 cm^{-1} are attributed to the C-H vibration of benzene ring. The peak at 1804 cm^{-1} is assigned to symmetric C=O stretch of carboxylic acid. The only difference between Figure 3b and Figure 3c is that the peaks of TiO₂ exist in Figure 3b. In addition, the monomer reactivity ratios in radical copolymerization for MAA and St are 0.7 and 0.15, respectively [26]. The MAA has a larger interaction force with TiO₂ than styrene, but the ratio of styrene is higher than that of MAA. Therefore, there are no homopolymers of MAA or St in the prophase of the reaction, and the shell is the copolymer of MAA with St. The monomer resides and the free polystyrene would be formed at the last stage. Thus we could say that poly(St-*co*-MAA) have precipitated on TiO₂ particle surface, and then TiO₂ core/poly(St-*co*-MAA) shell composite particles can be prepared by this method.

Thermal Analysis and Encapsulation Efficiency
Figure 4 was the TGA curve of (a) bare TiO₂, (b) the

Archive of SID

Zhang J. et al.   Preparation and Characterization of TiO₂ ...
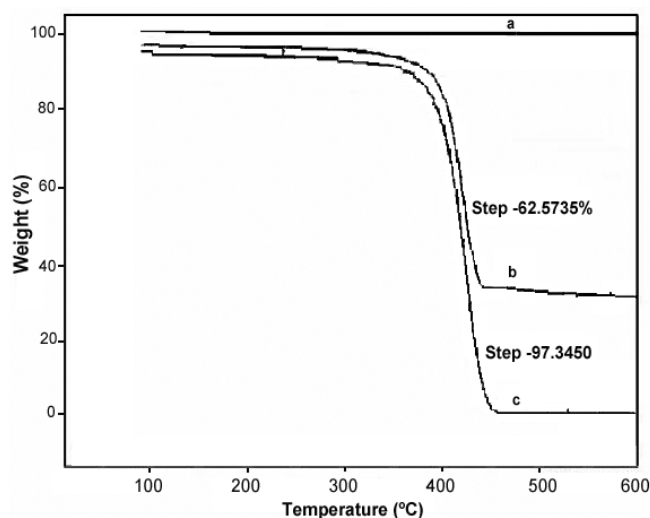
Figure 4. TGA Curves for: (a) bare TiO₂, (b) particles present in bottom phase of latex No. 3, and (c) polymer particles present in supernatant serum of latex No. 3.

composite sample No.3 and (c) the polymer particles No.3. As shown in Figure 4a, for bare TiO₂ there was not any weight loss when the temperature was lower than 600°C. However, the weight losses for the composite particles and the polymer particles were 62.6% and 97.3% respectively between the temperature of 250°C and 580°C. In this case, their weight loss was assigned to be the thermal decomposition of poly(St-*co*-MAA). Therefore, comparing Figure 3b with Figures 3a and 3c, the weight loss of the composite particles have indicated the surface of TiO₂ particles being coated with poly(St-*co*-MAA). This result was in agreement with the above-analyzed results of TEM and FTIR.

We used 3.0 g St and 2.0 g MAA to encapsulate 2.0 g TiO₂, and obtained 5.9 g dried particles. The conversion of monomers was 78.0%. From Figure 4b we have found the percentage of poly(St-*co*-MAA) in composite particles due to the thermal decomposition of composite particles was 62.6%, which was a little less than the theoretical value (71.4%) as a result of uncompleted reaction of the monomers and formation of polymer particles. It is calculated that the encapsulation efficiency is 85.8%.

CONCLUSION

The TiO₂ core and poly(St-*co*-MAA) shell composite

particles were prepared by emulsion polymerization. A particle size analysis and TEM result of the resulting composite particles showed that these particles were narrower in size distribution and regularly spherical core/shell morphology. The average particle diameter of composite particles was 191 nm. The encapsulation was best when the St/MAA weight ratio being 3/2, and the encapsulation efficiency was up to 85.8%. The conversion of monomers was 78.0% in this emulsion polymerization and copolymer of poly(St-*co*-MAA) was 62.6% in composite particles.

ACKNOWLEDGEMENTS

REFERENCES

1. Xie X.L., Li R.K., Liu Q.X., Mai Y.W., Structure-property relationships of in-situ PMMA modified nano-sized antimony trioxide filled poly(vinyl chloride) nanocomposites, *Polymer*, **45**, 2793-2802, 2004.
2. Rupali G., Amitabha D., Conducting polymer nanocomposites: A brief overview, *Chem. Mater.*, **12**, 608-622, 2000.
3. Vollath D., Szabo D.V., Schlabach S., Oxide/polymer nanocomposites as new luminescent materials, *J. Nanopart. Res.*, **6**, 181-191, 2004.
4. Srikanth H., Hajndl R., Chirinos C., Sanders J., Sampath A., Sudarshan T.S., Magnetic studies of polymer-coated Fe nanoparticles synthesized by microwave plasma polymerization, *Appl. Phys. Lett.*, **79**, 3503-3505, 2001.
5. Sung J.H., Jang I.B., Choi H.J., Chin I.J., Titania-coated polystyrene spheres for electronic ink, *Polym. Prepr.*, **45**, 970-971, 2004.
6. Chen J., Wang G., Zeng X., Zhao H., Toughening of polypropylene-ethylene copolymer with nanosized CaCO₃ and styrene-butadiene-styrene, *J. Appl. Polym. Sci.*, **94**, 796-802, 2004.
7. Abboud M., Casaubieilh L., Morvan F., Fontanille M., Duguet E., PMMA-based composite materials with reactive ceramic fillers: IV. Radiopacifying

particles embedded in PMMA beads for acrylic bone cements, *J. Biomed. Mater. Res. Part A*, **53**, 728-736, 2000.

8. Bauer F., Glasel H.J., Hartmann E., Bilz E., Mehnert R., Surface modification of nanoparticles for radiation curable acrylate clear coatings, *Nucl. Instru. Methods Phys. Res., Sec. B*, **208**, 267-270, 2003.

9. Norio S., Makoto F., Yoshinari T., Masato T., The effect of surface treatment of agnetite powder on a structure of composite particles prepared by suspension polymerization, *J. Chem. Eng. Jpn.*, **37**, 731-736, 2004.

10. Erdem B., Sudol E.D., Dimonie V.L., Mohamed S., Encapsulation of inorganic particles via miniemulsion polymerization characterization of encapsulation, *J. Polym. Sci. Part A*, **38**, 4441-4450, 2000.

11. Caruso F., Nanoengineering of particle surfaces, *Adv. Mater.*, **13**, 11-22, 2001.

12. Luna-Xavie J.L., Guyot A., Bourgeat-Lami E., Synthesis and characterization of silica/poly (methyl methacrylate) nanocomposite latex particles through emulsion polymerization using a cationic azo initiator, *J. Colloid Interface Sci.*, **250**, 82-92, 2002.

13. Yu D.G., An J.H., Bae J.Y., Lee Y.E., Preparation and characterization of titanium dioxide core/polymer shell hybrid composite particles prepared by emulsion polymerization, *J. Appl. Polym. Sci.*, **92**, 2970-2975, 2004.

14. Yu D.G., An J.H., Bae J.Y., Ahn S.D., Kang S.Y., Suh K.S., Preparation of titanium dioxide/poly(methyl methacrylate-*co*-n-butylacrylate-co-methacrylic acid) hybrid composite particles via emulsion polymerization, *J. Appl. Polym. Sci.*, **97**, 72-79, 2005.

15. Yu H.Y., Gu J.S., Guan M.Y., Wu Z.C., Sun Y.M., Du J., Surface modification of nano-SiO₂ by grafting PMMA/PBA, *Chin. J. Chem.*, **21**, 1297-1299, 2003.

16. Viala P., Bourgeat-Lamy E., Guyot A., Legrand P., Lefebvre D., Pigment encapsulation by emulsion polymerisation, redispersible in water, *Macromol. Symp.*, **187**, 651-661, 2002.

17. Choi S.H., Choi M.S., Lee K.P., Kang H.D., Prevaration and characterization of CdS and

CdS/polyacrylonitrile nanocomposites by gamma-irradiation and emulsion polymerization, *J. Appl. Polym. Sci.*, **91**, 2335-2342, 2004.

18. Tan D.S., Yan N.X., Xue Q., Study on surface modification of titanium dioxide using poly-methylethacrylate, *J. Shanghai Univ.*, **2**, 67-71, 1998.

19. Duguet E., Morvan F., Maheu P., Fontanille M., Abboud M., PMMA Encapsulation of alumina particles through aqueous suspension polymerisation processes, *Macromol. Symp.*, **151**, 365-370, 2000.

20. Dong-Guk Y., Jeong H.A., Titanium dioxide core/polymer shell hybrid composite particles prepared by two-step dispersion polymerization, Colloids Surf. A: *Physicochem. Eng. Aspects*, **237**, 87-93, 2004.

21. Yu D.G, An J.H, Preparation and characterization of titanium dioxide core and polymer shell hybrid composite particles prepared by two-step dispersion polymerization, *Polymer*, **45**, 4761-4768, 2004.

22. Yu D.G., An J.H., Bae J.Y., Kim S., Lee Y.E., Ahn S.D., Kang S.Y., Suh K.S., Carboxylic acid functional group containing inorganic core/polymer shell hybrid composite particles prepared by two-step dispersion polymerization, *Colloids Surf. A: Physicochem. Eng. Aspects*, **245**, 29-34, 2004.

23. Wu R., Wei Y., Zhang Y.F., A preparation of nano-sized TiO₂ particles by forced hydrolysis from titanium salt, *Mater. Res. Bull.*, **34**, 2131-2135,1999.

24. Corcos F., Bourgeat-Lami E., Novat C., Lang J., Poly(styrene-*b*-ethylene oxide) copolymers as stabilizers for the synthesis of silica-polystyrene core-shell particles, *Colloid. Polym. Sci.*, **277**, 1142-1151, 1999.

25. Zeng Z., Yu J., Guo Z.X., Preparation of functionalized core-shell alumina/polystyrene composite nanoparticles, 1-Encapsulation of alumina via emulsion polymerization, *Macromol. Chem. Phys.*, **206**, 1558-1567, 2005.

26. Odian G., *Principles of Polymerization*, John Wiley, New York, 452, 1981.