

NETWORK ENCAPSULATION OF NANOMETER CaCO_3

Wen-fang Liu, Jian Yu* and Zhao-xia Guo

*Institute of Polymer Science and Engineering, Department of Chemical Engineering,
School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

Abstract The encapsulation of stearic acid coated nanometer CaCO_3 by a polystyrene (PS) network via emulsion polymerization is described, where γ -methacryloxypropyltrimethoxysilane (MPS) was used as an efficient crosslinker. The important factors such as the type and amount of surfactant and initiator and the content of CaCO_3 are investigated as well as the role of MPS. It has been shown that little PS was extractable with only 0.6 wt% of MPS (relative to styrene). The cationic surfactant cetyl trimethylammonium bromide (CTAB) proved more effective than the anionic surfactant sodium dodecyl sulfonate (SDS). The yield rises, particles become smaller and size distribution broadens with increased amount of CTAB. It is also found that either 2,2'-azobis(isobutyronitrile) (AIBN) or ammonium persulfate (APS) is suitable for attaining high monomer conversion. With increased amount of CaCO_3 , the encapsulation ratio can be varied from 17.9 to 3.6, while monomer conversion and yield decrease slightly. FT-IR spectra of the products after extraction indicate tight encapsulation between PS and CaCO_3 , and TEM photographs of composite particles with well-defined core-shell structure give direct evidence of encapsulation.

Keywords Calcium carbonate, Polystyrene, Network, Encapsulation, Nanocomposite particles

INTRODUCTION

In recent years, increasing attention has been paid to synthesis of polymer/inorganic composite nanoparticles since such composite materials are expected to combine properties of both inorganic nanoparticles and organic molecules. The core can give mechanical strength or some special properties and the shell can confer compatibility with the surrounding medium. For example, Haga *et al.*^[1] reported interesting light-sensitive effects of zinc oxide and cadmium sulfide encapsulated by polymethylmethacrylate (PMMA) obtained through soapless emulsion polymerization.

In fact, for inorganic fillers with extensive applications, especially those in nanometer size, the preparation of composite particles through polymerization is an efficient way to prevent their agglomeration and improve mechanical properties. Encapsulation of silica^[2–7] has been extensively studied; however, only few studies^[8–10] concern calcium carbonate.

Yang *et al.*^[8] employed soapless emulsion polymerization to encapsulate CaCO_3 ; however, only 6.4% polystyrene (PS) remained after Soxhlet extraction with toluene. Janssen *et al.*^[9] encapsulated CaCO_3 pretreated with alkanolamine titanate using emulsion polymerization, and the tightly bonded PS/ CaCO_3 are less than 10%. Bechthold *et al.*^[10] first precoated CaCO_3 with a layer of stearic acid (SA) in order to provide a hydrophobic surface and improve its dispersibility in the monomer phase, then obtained composite particles through miniemulsion polymerization.

However, the studies mentioned above only provided weakly encapsulated micrometer particles. On one hand, desorption of the polymer covering the particles can easily occur when the conditions of pH and ionic strength are changed^[11]; on the other hand, encapsulated polymer tends to melt or dissolve when composite

* Corresponding author: Yu Jian (于建), E-mail: yujian03@mail.tsinghua.edu.cn

Received September 8, 2003; Revised September 25, 2003; Accepted September 29, 2003

particles are subjected to heat or solvent treatment. There are two ways of obtaining more stable encapsulation^[11]. One concerns the use of a coupling agent containing a double bond or an initiator moiety. Bourgeat-Lami *et al.*^[3] have grafted poly(ethyl acrylate) onto silica, which has beforehand been functionalized by reaction with methacryloxypropyltrimethoxysilane (MPS) carrying a double bond. As a result, unextractable polymer is up to 48%. Our group has followed a similar approach in encapsulation of CaCO₃ by PS, and only 4% polymer is extractable by xylene^[12]. The second way is by the addition of a small amount of crosslinker, for example, ethylenebisacrylamide has been used for preparing poly(acrylamide)/iron oxide composite particles^[13]. In this work, MPS are used as a crosslinker to achieve strong encapsulation of SA coated nanometer CaCO₃ by PS. Common chemical reactions between the silanes and the reactive surface impurities of CaCO₃, such as Ca(OH)₂ seem impossible since the surface of CaCO₃ is covered by a layer of SA. Therefore, MPS cannot be used as a coupling agent to introduce polymerizable double bond onto the surface of CaCO₃. MPS has a double bond and three siloxane groups, can undergo copolymerization with styrene (St) and at the same time condensation can take place between methoxyl groups of different MPS molecules. In this way, MPS is capable of helping to form a polymer network on the surface of nanometer CaCO₃ via emulsion polymerization. In this paper, we discuss the role of MPS and the influence of some factors on encapsulation.

EXPERIMENTAL

Materials

Nanometer CaCO₃ is a gift from Mengxi High-tech & New Material Co. Ltd. in Wuhai City in Inner Mongolian Municipality (China), and its fundamental physical and chemical properties are listed in Table 1. Styrene is distilled under reduced pressure before use. 2,2'-Azobisisobutyronitrile (AIBN) and ammonium persulfate (APS) were recrystallized from ethanol and water, respectively. Methacryloxypropyltrimethoxysilane (MPS), cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulfonate (SDS) and poly(ethylene glycol) decyl phenyl ether (OP-10) were used as supplied.

Table 1. Physical and chemical properties of CaCO₃

Particle size (nm) ^a	Density (g/cm ³)	Specific surface area (m ² /g)	pH	Zeta potential
30–65	2.6	44	8.7	–15.5

^a Obtained from TEM

Emulsion Polymerization

A 250 mL four-necked flask equipped with reflux condenser, thermometer, mechanical stirrer and N₂ inlet, was charged with deionized water (60 g), cationic surfactant CTAB (0.1 g to 0.8 g) and nonionic surfactant OP-10 (0.1 g). The temperature of the mixture was raised to 60 °C. A mixture of styrene (15 mL), AIBN (0.03 g to 0.2 g) as the initiator and stearic acid coated CaCO₃ (1 g to 4 g) was added after ultrasonic treatment for 10 min. After stirring for 20 min at 60 °C, the temperature was raised to and held at 80 °C for 1.5 h, then raised to and held at 90 °C for half an hour. A part of the emulsion was poured into a beaker and de-emulsified with hot ethanol. The product was collected by suction filtration, washed with hot water, and then dried.

Characterization

High-Resolution Pyrolysis Gas Chromatography (HRPGC) was performed on a PYR-2A pyrolyzer, which was directly attached to a gas chromatograph (Shimadzu GC-14B) with a fused-silica capillary column (SGE AC-5, 25 m × 0.25 mm i.d.) and FID. The sample was pyrolyzed at 600 °C, and the column temperature was programmed from 50 °C (held for 1 min) to 220 °C at a rate of 8 K/min. Here nitrogen was used as carrier gas at a flow rate of 50 mL/min. Thermogravimetric analysis (TGA) was carried out on a TA 2050 instrument with a heating rate of 20 K/min in flowing N₂. Infrared (IR) spectra were recorded on a Nicolet 560 FT-IR spectrometer. The morphologies of original powder and composite particles are observed using a Philips CM 120 electron microscope. For transmission electron microscopy (TEM) experiments, a highly diluted dispersion of the sample, made from emulsion diluted with water or a powder sample dispersed in ethanol, was cast on a carbon-

coated copper grid and allowed to dry. Particle size ($\bar{D}_p$) and polydispersity index (PDI) of latex were measured with a Zetasizer HS 3000 laser light scattering instrument of Malvern Co. Ltd., by what which was commonly called the dynamic light scattering (DLS) method. PDI is close to zero (0.000 to 0.020) for monodisperse or nearly monodisperse samples, small (0.020 to 0.080) for narrow distributions, and larger for boader distributions.

Monomer conversion is determined by a gravimetric method. In order to estimate the strength between encapsulated polymer and CaCO_3 , the product was extracted with xylene for 12 h using a Soxhlet apparatus. The yield, encapsulating ratio and extractable PS were calculated as follows:

$$\text{Yield (\%)} = \frac{\text{Product before extraction (g)}}{\text{Total monomer (g) and CaCO}_3 \text{ (g)}} \times 100 \quad (1)$$

$$\text{Encapsulating ratio} = \frac{\text{Overall polymer (g)}}{\text{CaCO}_3 \text{ (g)}} \quad (2)$$

$$\text{Extractable PS (\%)} = \frac{\text{Polystyrene removed by xylene (g)}}{\text{Polystyrene formed (g)}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

The Role of MPS

Figure 1 shows effect of the amount of MPS on extractable PS. Encapsulated polymer was entirely extractable without MPS, while only 17.6% PS was extractable when 0.2 wt% (relative to styrene) of MPS was added. The value decreased to 2.6% when the amount of MPS was increased to 0.6 wt%. So it is apparent that the introduction of MPS changes to a large extent the encapsulation state of PS from physically entangled stack to crosslinked networks.

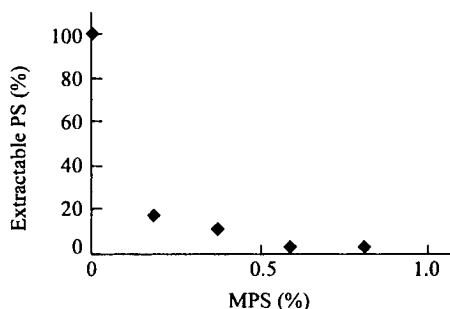


Fig. 1 Percentage of extractable PS as a function of the amount of MPS, in this case, the weight ratio of $\text{CaCO}_3/\text{CTAB}/\text{OP}/\text{AIBN}/\text{St}$ is 7.3/3.7/0.7/0.7/100.

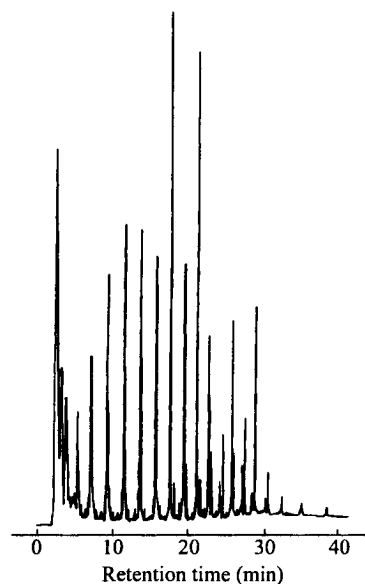


Fig. 2 HRPGC of stearic acid coated CaCO_3

In order to check the role of MPS, we went through the same polymerization procedure in the presence of an inhibitor benzoquinone and without initiator, and then CaCO_3 was isolated by suction filtration and extracted in a

Soxhlet apparatus for 12 h with xylene. The HPLC graph of the dried powder was found to be the same as that of original CaCO_3 , which is shown in Fig. 2. Stearic acid or stearate is detected on the surface of CaCO_3 , in fact, the amount is 7 wt% (relative to CaCO_3), determined by means of TGA (Fig. 3). The results prove that no reaction takes place between stearic acid coated CaCO_3 and MPS. This means that MPS cannot serve as a coupling agent in this system. As mentioned above, the use of MPS gives tight encapsulation, indicating that MPS is serving as a crosslinker.

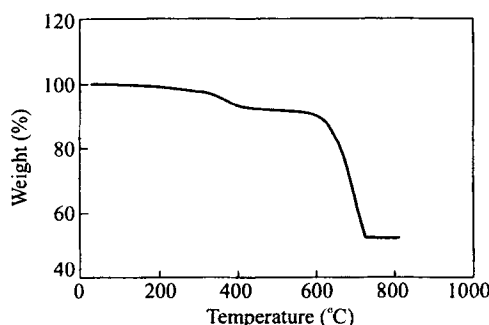


Fig. 3 TGA of stearic acid coated CaCO_3

Effect of Surfactant

In this work, a mixture of ionic surfactant and non-ionic surfactant OP are used, of which the former is the major surfactant. In order to select an appropriate major surfactant for encapsulation of CaCO_3 , two different types of surfactants are compared and several fundamental parameters and experimental phenomena are summarized in Table 2. We can conclude that the cationic surfactant CTAB is more favorable than the anionic surfactant SDS since no agglomerate is observed in the system with CTAB while a large amount of agglomerates occur in the system with SDS. The reason is supposed to be related to the basic character of the surface of CaCO_3 . As seen in Table 1, the zeta potential of the surface of CaCO_3 is negative, namely, CaCO_3 carries negative charges, and thus electrostatic attractions are likely to take place between the surface of CaCO_3 and the cationic ammonium groups when CTAB is used as the surfactant. In order to investigate the dependence of the yield and particle size on the amount of the surfactant, the amount of CTAB was systematically varied over a wide range. As shown in Table 3, the yield rises and particles become smaller with wider size distribution, which are in accordance with usual emulsion polymerization.

Table 2. Comparison between two different surfactants^a

Surfactant	SDS	CTAB
Yield (%)	–	87.0
$\bar{D}_p^b$ (nm)	–	84
PDI ^b	–	0.230
Phenomena	There are a large amount of agglomerates occurring soon after reaction starts.	The system is stable and no agglomerate is observed.

^a The weight ratio of CaCO_3 /MPS/CTAB/OP/AIBN/St is 7.3/0.6/6/0.7/1.1/100;

^b Determined by DLS method

Table 3. Effect of the amount of CTAB on polymerization^a

Entry	CTAB (wt%)	Yield (%)	$\bar{D}_p$ (nm)	PDI
1	1	60.1	152	0.003
2	2.9	73.9	110	0.006
3	3.7	78.5	97	0.020
4	6	87.0	84	0.230

^a Formulation is the same as Table 2, except for the amount of CTAB.

Effect of the Amount of AIBN

The dependence of monomer conversion and yield on the amount of AIBN is described in Fig. 4. It is clear that monomer conversion and yield both reached maximum when the ratio of AIBN to St was in the range of 0.3%–1.5%.

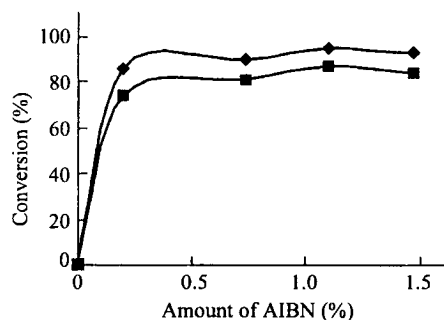


Fig. 4 Effect of the amount of AIBN on monomer conversion and the yield, weight ratio of CaCO_3 /MPS/CTAB/OP/St is 7.3/0.6/6/0.7/100

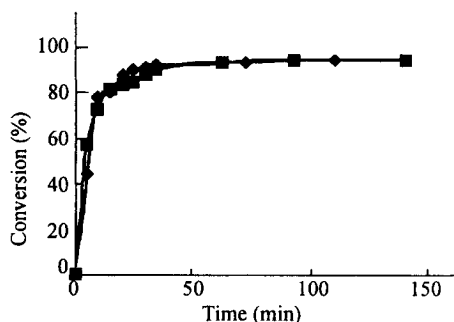


Fig. 5 Kinetic curves of polymerization with different initiators, weight ratio of CaCO_3 /MPS/CTAB/OP/St is the same as in Fig. 4

Kinetics of Emulsion Polymerization with Different Initiators

As shown in Fig. 5, the kinetic curves of the emulsion polymerization with either oil-soluble initiator (AIBN) or water-soluble APS are very similar. The rate of polymerization was quick at the earlier stage. The monomer conversion could reach 80% in 15 min and climb to 90% when the reaction proceeded for 35 min. After that, the value rose slowly and it was up to 95% when reaction ended after 140 min. This indicates that both AIBN and APS can be used for encapsulation of CaCO_3 by PS network through emulsion polymerization.

Effect of the Content of CaCO_3

In order to investigate the influence of the content of CaCO_3 on encapsulation, we changed it from 7.3% to 58.7% (relative to St). The results are listed in Table 4. It is clear that both monomer conversion and yield had a decreasing trend when the content of CaCO_3 increased. The influence of CaCO_3 on emulsion polymerization is two-fold: the presence of CaCO_3 can stabilize the emulsion system, which is attributed to the ionic character of the surface (without CaCO_3 , a large amount of agglomerations are observed), and at the same time it may inhibit polymerization to a certain extent. In addition, the encapsulation ratio varies from 17.9 to 3.6, which gradually approaches the calculated value.

Table 4. Encapsulation of CaCO_3 by PS^a

Entry	CaCO_3 /monomer (wt%)	Monomer conversion (%) ^b	Yield (%)	Encapsulation ratio	
				Calculated value	Real value ^c
4	7.3	95.0	87.0	13.6	17.9
5	14.7	92.4	82.3	6.8	8.5
6	29.3	86.4	77.0	3.5	3.6
7	58.7	74.4	66.9	1.8	1.9

^a Formulation is the same as in Table 2; ^b Determined by gravimetric method; ^c Determined by means of TGA

FT-IR Spectra of the Product after Extraction

Figure 6 shows FT-IR spectra of original CaCO_3 and Sample Entry 5 after extraction. The absorption peaks at 3000–3100, 1600, 1493, 756 and 698 cm^{-1} are the characteristic peaks of polystyrene, indicating tight encapsulation between PS and CaCO_3 , as any physically adsorbed polymer has been removed by Soxhlet extraction with xylene prior to the IR measurement. Also, it is noted that the peaks at the region of 1400–1500 cm^{-1} and 875.5 cm^{-1} , which are assigned to the characteristic vibrations of the carbonate, become stronger with increased amount of CaCO_3 when the characteristic peaks of polystyrene at 3000–3100 cm^{-1} have been adjusted to the same level, indicating more CaCO_3 is involved.

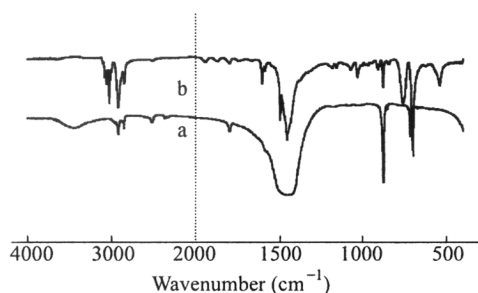


Fig. 6 FT-IR spectra of (a) original CaCO_3 and (b) sample Entry 5 after extraction

TEM Photographs of Composites

As direct evidence of encapsulation, TEM photographs of composites are shown in Fig. 7. It can be seen that the shape of original particles (Fig. 7a) is irregular with a particle size of 30–65 nm. After encapsulation, the particles become spherical in shape and bigger in size (60–70 nm, Fig. 7b). More importantly, they show core-shell morphology, indicating the occurrence of encapsulation. It is noted that some particles appear smaller in size and lighter in brightness than most of the others in Fig. 7(b), indicating that a small amount of free polymer particles exists in this system.

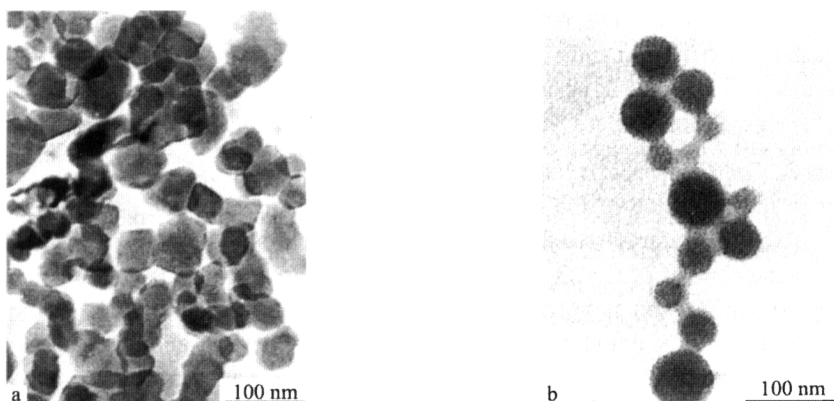


Fig. 7 TEM photographs of (a) original CaCO_3 and (b) composite particles (Sample Entry 5)

CONCLUSIONS

Stearic acid coated nanometer calcium carbonate was successfully encapsulated by polystyrene network via emulsion polymerization, where MPS was not used as a coupling agent but as an efficient crosslinker. CTAB is proved more effective than SDS and either AIBN or APS is suitable for attaining high monomer conversion. The influence of CaCO_3 on the emulsion polymerization is two fold: the presence of CaCO_3 can stabilize the emulsion system with cationic surfactant owing to the ionic character of the surface and at the same time it may inhibit polymerization to a certain extent. FT-IR spectra of the products after extraction indicate tight encapsulation between PS and CaCO_3 , and TEM photographs of composite particles with well-defined core-shell structure give direct evidence of encapsulation.

REFERENCES

- 1 Haga, Y., Watanabe, R. and Yosomiya, R., *Angew. Makromol. Chem.*, 1991, 188: 73
- 2 Furusawa, K., Kimura, Y. and Tagawa, T., *J. Colloid Interface Sci.*, 1986, 109: 69

- 3 Espiard, Ph. and Guyot, A., *Polymer*, 1995, 36(23): 4391
- 4 Bourgeat-Lami, E. and Lang, J., *J. Colloid Interface Sci.*, 1998, 197(2): 293
- 5 Werne, T. and Patten, T.E., *J. Am. Chem. Soc.*, 1999, 121: 7409
- 6 Bourgeat-Lami, E. and Lang, J., *Macromol. Symp.*, 2000, 151: 337
- 7 Yu, J., Yu, J. and Gao, Y.F., *Chin. J. Polym. Sci.*, 2002, 20(1): 71
- 8 Yang, Y., Kong, X.Z., Kan, C.Y. and Sun, C.G., *Polym. Adv. Technol.*, 1999, 10(1–2): 54
- 9 Janssen, E.A.W.G., Herk, A.M. and German, A.L., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1993, 34: 532
- 10 Bechhold, N., Tiarks, F., Willert, M., Landfester, K. and Antonietti, M., *Macromol. Symp.*, 2000, 151: 549
- 11 Bourgeat-Lami, E., Espiard, Ph. and Guyot, A., *Polymer*, 1995, 36(23): 4385
- 12 Yu, J., Yu, J., Guo, Z.X. and Gao, Y.F., *Macromol. Rapid Commun.*, 2001, 22(15): 1261
- 13 Huang, I.C.C., “The Model Encapsulation of Iron Oxides in Latex Particles by Preparation and Characterization of Magnetic Latex Particles”, Ph. D. Thesis, Lehigh Univ., 1986