Journal of Zhejiang University SCIENCE
ISSN 1009-3095
http://www.zju.edu.cn/jzus
E-mail: jzus@zju.edu.cn

Preparation of poly (methyl methacrylate)/nanometer calcium carbonate composite by in-situ emulsion polymerization*

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Received July 4, 2003; revision accepted Oct. 28, 2003

Abstract: Methyl methacrylate (MMA) emulsion polymerization in the presence of nanometer calcium carbonate (nano-$CaCO_3$) surface modified with γ-methacryloxypropyltrimethoxysilane (MPTMS) was carried out to prepare poly (methyl methacrylate) (PMMA)/nano-$CaCO_3$ composite. The reaction between nano-$CaCO_3$ and MPTMS, and the grafting of PMMA onto nano-$CaCO_3$ were confirmed by infrared spectrum. The grafting ratio and grafting efficiency of PMMA on nano-$CaCO_3$ modified with MPTMS were much higher than that on nano-$CaCO_3$ modified with stearic acid. The grafting ratio of PMMA increased as the weight ratio between MMA and nano-$CaCO_3$ increased, while the grafting efficiency of PMMA decreased. Transmission electron micrograph showed that nano-$CaCO_3$ covered with PMMA was formed by in-situ emulsion polymerization.

Key words: Methyl methacrylate, Nanometer calcium carbonate, Emulsion polymerization, γ-methacryloxypropyltrimethoxysilane, Grafting
Document code: A **CLC number:** TQ316.334

INTRODUCTION

In recent decades, extensive research efforts have been directed towards the preparation and characterization of polymer/inorganic nanometer particles composite (Siegel, 1994). Nanometer inorganic particles easily agglomerate because of their high surface energy, so it is difficult to achieve the homogeneous dispersion of nanoparticles in polymer matrix. Surface modification of an inorganic particle with an organic substance is a useful way to reduce its surface energy, to increase its compatibility with polymer matrix and the dispersion homogeneity, and thus to improve the properties of the polymer/inorganic particles nanocomposite.

Emulsion polymerization has been widely used to modify inorganic particles with polymer. Surfactant-free emulsion polymerizations of vinyl monomers in the presence of various inorganic particles were carried out by Hasegawa *et al.*(1987a; 1987b), Hergeth *et al.*(1988; 1989) and Caris *et al.*(1989). In most cases, the surface of particles is partially or totally covered with polymer mainly through static electric forces. The remarkable improvement in properties of nanocomposite can be achieved when some polymer chains are covalently bonded to inorganic nanoparticles (Baraton *et al.*,

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* Project (No. 01101619) supported by the Science and Technology Project of Zhejiang Province, China

1997; Espiard and Guyot, 1995; Espiard *et al.*, 1995; Hayashi *et al.*, 1999; Liu *et al.*, 1998).

Although encapsulation of silica with polymer has been extensively studied, only few studies concern calcium carbonate. Janssen *et al.*(1993) employed emulsion polymerization to encapsulate $CaCO_3$ pretreated with titanate, and found that less than 10% of polystyrene produced was chemically bonded at the surface of $CaCO_3$. Yang *et al.*(1999) obtained composites of $CaCO_3$ encapsulated by polystyrene using soapless emulsion polymerization. The encapsulating ratio was 60%, but only 6.4% remained after Soxhlet extraction with toluene.

In this work, in-situ emulsion polymerizations of methyl methacrylate in the presence of nanometer $CaCO_3$ pretreated with γ-methacryloxypropyltrimethoxysilane were carried out to prepare poly (methyl methacrylate)/nanometer $CaCO_3$ composite.

EXPERIMENTAL DETAILS

Material

Methyl methacrylate (MMA), purchased from Yuhang Co., China, was distilled under reduced pressure. Nanometer $CaCO_3$ (nano-$CaCO_3$) was donated by ACCR Co. Ltd, Hangzhou, and had average particle diameter of about 50 nm. Nano-$CaCO_3$ modified with stearic acid was also donated by ACCR Co. Ltd. γ-methacryloxypropyltrimethoxysilane (MPTMS) from Shuguang Company was of chemical purity. 2,2'-Azoisobutyronitrile (AIBN) and sodium dodecyl sulfate (SDS) were of analytical purity and used as received.

Surface modification of nano-$CaCO_3$

Nano-$CaCO_3$ was dried under vacuum (2 kPa) at 100 °C for 20 h to remove physically adsorbed species before modification. The introduction of reactive groups onto $CaCO_3$ surface was achieved by the reaction of MPTMS with the hydroxyl groups of $CaCO_3$. A typical process was as follows: 30 g $CaCO_3$ and 200 ml pure toluene were placed into a flask equipped with a stirrer. MPTMS (5 wt% to $CaCO_3$) was added dropwisely under rapid stirring. The slurry was left standing in the flask for 2 days. The solvent was removed under vacuum at 60 °C. The modified nano-$CaCO_3$ was dried and ground, then stored at room temperature for 3 days before use.

Emulsion polymerization

Polymerizations were carried out using a 500 ml jacketed glass reactor fitted with a stirrer, reflux condenser, thermometer and N_2 inlet. The pretreated nano-$CaCO_3$, 200 ml distilled water and SDS were put into the reactor after ultrasonic treatment for 10 min. The concentration of SDS was 1.0 g/L to water, which was much lower than its critical micelle concentration (CMC). After the addition of initiator solution and monomer, the mixture was raised to 60 °C, and maintained at this temperature for 5 h under N_2 atmosphere.

The reaction mixture was then centrifuged at 4000 rev/min for 10 min, and the sediment was dispersed in deionized water again using mechanical agitation and ultrasonic bath, this centrifugation-dispersion cycle was repeated two to five times. Finally, the composite was collected, dried and ground into powder.

Characterization

A drop of a diluted dispersion was put on a carbon film supported by a copper grid and dried in the vacuum chamber of a JEM-1200EX electron microscope. The morphology of nano-$CaCO_3$ particles and PMMA/nano-$CaCO_3$ composite particles was observed by using TEM.

The product was extracted with toluene for more than 20 h to remove the ungrafted PMMA completely. The weight loss of the original nano-$CaCO_3$, silane modified nano-$CaCO_3$ and PMMA/nano-$CaCO_3$ composite was determined by using a Perkin Elmer TGA thermogravimetric instrument under N_2 atmosphere. The heating rate was 10 °C/min.

The conversion of MMA monomer to polymer was determined gravimetrically. The grafting ratio (f_r) and efficiency of PMMA (f_e) were calculated as follows:

$$f_{\rm r} = \frac{\text{PMMA unremoved by extraction (g)}}{\text{CaCO}_3\ \text{added (g)}} \times 100\%$$

$$f_{\rm e} = \frac{\text{PMMA unremoved by extraction (g)}}{\text{PMMA formed (g)}} \times 100\%$$

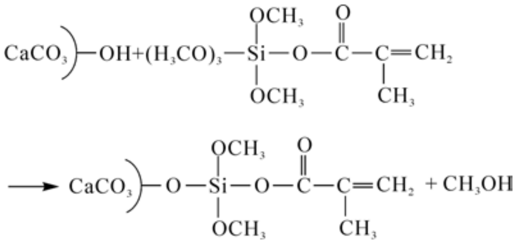
RESULTS AND DISCUSION

Modification of nano-$CaCO_3$

The introduction of C=C group onto $CaCO_3$ surface was achieved by the reaction described in Fig.1.

The existence of free –OH group on the surface of $CaCO_3$ was confirmed by its infrared (IR) spectrum shown in Fig.2, in which an obvious adsorption at 3432 cm^{-1} is shown. The content of –OH group of $CaCO_3$ was determined to be 0.42 mmol/g by measuring volumetrically the amount of hydrogen evolved by reaction with triethylaluminum.

Nano-$CaCO_3$ pretreated with MPTMS was Soxhlet-extracted with toluene for 24 h. Thermogravimetric analysis (TGA) showed that 52.2% (2.61 wt% to $CaCO_3$) of MPTMS remained after extraction. The IR spectrum of the extracted sample (2 in Fig.2) showed adsorptions at 2931.1 cm^{-1} (ν-CH_3), 1124.5 cm^{-1} (ν-COOR) and 812.7 cm^{-1} (νC(CH_3)=CH_2). This clearly indicated the existence of chemically bonded MPTMS on the $CaCO_3$ surface. Thus, the inert $CaCO_3$ surface can become active part and act with MMA like a comonomer in the polymerization.



$$\text{CaCO}_3\text{—OH} + (\text{H}_3\text{CO})_3\text{—Si(OCH}_3)_2\text{—O—C(=O)—C(CH}_3)\text{=CH}_2 \longrightarrow \text{CaCO}_3\text{—O—Si(OCH}_3)_2\text{—O—C(=O)—C(CH}_3)\text{=CH}_2 + \text{CH}_3\text{OH}$$

Fig.1 Introduction of MPTMS onto $CaCO_3$ particle

Influence of surface modification of nano-$CaCO_3$ on the grafting of PMMA

Emulsion polymerization of MMA was carried out in the presence of modified $CaCO_3$ with different weight ratios between $CaCO_3$ and MMA. The formation of PMMA grafted to $CaCO_3$ particles is confirmed by the IR spectrum shown in Fig.3, in which absorptions at 750.5 cm^{-1} (ν=CH_2), 1147.7 cm^{-1} (ν-C-O), 1732.1 cm^{-1} (ν-C=O) and 2951.8 cm^{-1} (ν-CH_3) indicate existence of PMMA.

The applied SDS concentration in the present emulsion polymerization system was much lower than its CMC, so few latex particles without $CaCO_3$ particles would be formed. During the polymerization process, the oligomers formed at the early stage of emulsion polymerization behaved like surface-active agents and were adsorbed on the $CaCO_3$ surface, then the monomer molecules and radicals in the water phase were also be adsorbed onto the surface layer formed by the oligomers. As a result, the polymerization locus transferred from

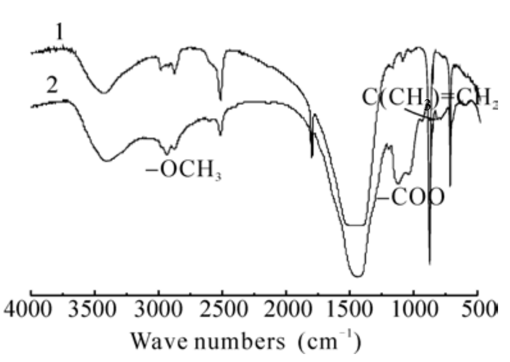


Fig.2 IR spectrum of original nano-$CaCO_3$ (1) and nano-$CaCO_3$ modified with MPTMS (2)

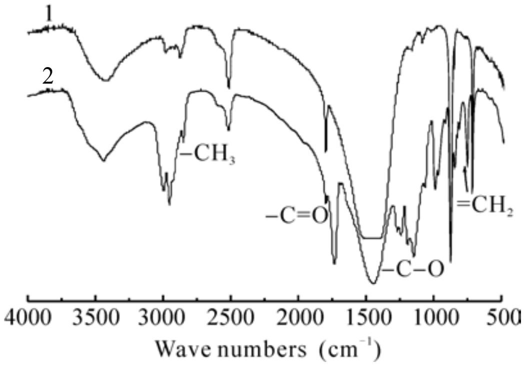


Fig.3 IR spectrum of original $CaCO_3$ (1) and PMMA/$CaCO_3$ composite (2)

the aqueous phase to the powder surface at the early stage of the reaction, and C=C bond of MPTMS would react with MMA to form grafted PMMA.

Influence of the modifier type and the weight ratio between $CaCO_3$ and MMA on the polymerization conversion, f_r and f_e of the resulted composite is shown in Table 1, showing that the existence of nano-$CaCO_3$ in the polymerization system affects the final conversion of MMA (the conversion of MMA is 96% for polymerization with no nano-$CaCO_3$). The conversion of MMA decreased as more $CaCO_3$ was added. When nano-$CaCO_3$ pretreated with stearic acid was used in the polymerization, most of the formed PMMA could be easily removed by Soxhlet extraction, and grafting ratio of PMMA was much lower. However, relatively higher grafting ratio was achieved when MPTMS pretreated $CaCO_3$ was used in the in-situ emulsion polymerization. It can also be seen that the grafting efficiency decreased as more MMA was added.

Thermogravimetric analysis

Fig.4 shows TGA plots of original $CaCO_3$ (curve 1), pure PMMA (curve 2) and different extracted PMMA/$CaCO_3$ composites. The original $CaCO_3$ did not decompose below 550 °C and the weight loss was 1.2% above 550 °C. Curve 2 shows that pure PMMA decomposes completely above 550 °C and that the remained weight was 4.63%. For PMMA/$CaCO_3$ composite, the weight loss between 250 °C to 550 °C was attributed to the existence of encapsulating PMMA. TGA of extracted PMMA/$CaCO_3$ composites revealed weight loss of 94.05%, 78.13%, 80.18%, 84.57% for sample 1 to sample 4 in Table 1, respectively. From the conversions of MMA and the weight loss of extracted PMMA/$CaCO_3$ composites, the grafting ratio and grafting efficiency of PMMA can be calculated as shown in Table 1.

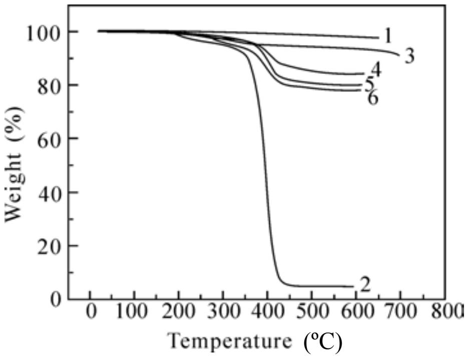


Fig.4 TGA plot of original $CaCO_3$ (curve 1), pure PMMA (curve 2) and PMMA/$CaCO_3$ composite after extraction (curve 3, 4, 5 and 6 correspond to the sample 1, 2, 3, 4 in Table 1)

Electron microscopy

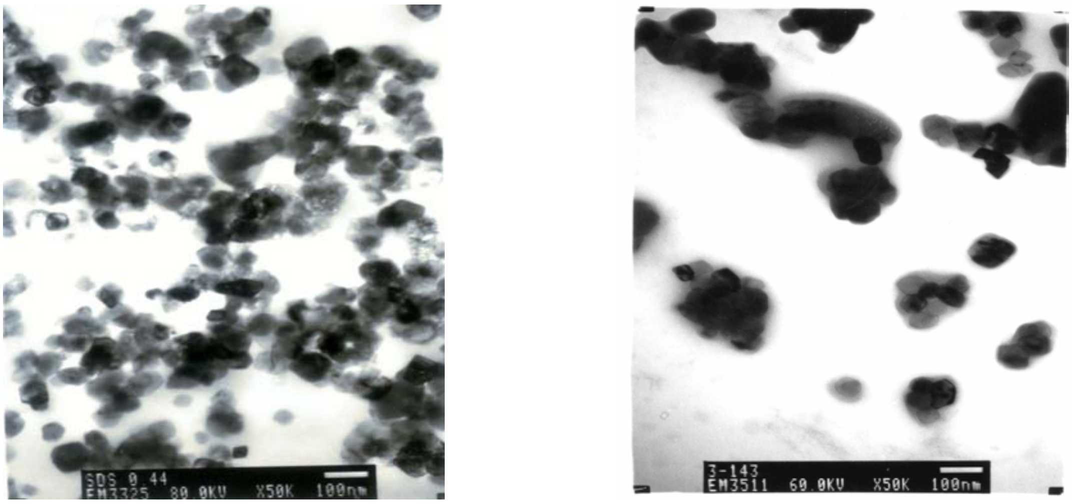
Fig.5 shows TEM photographs of original nano-$CaCO_3$ (a) and PMMA/$CaCO_3$ composite (b) taken from the emulsion system after the polymerization. The average size of primary particles of original nano-$CaCO_3$ was about 50 nm. TEM photograph of PMMA/$CaCO_3$ composite shows the encapsulation of PMMA on $CaCO_3$ with each composite particle encapsulating more than one $CaCO_3$ primary particle. This was caused by the agglomeration of the original $CaCO_3$ particles.

CONCLUSIONS

PMMA/nano-$CaCO_3$ composite with higher grafting efficiency of PMMA was successfully prepared by emulsion polymerization of MMA in the presence of nano-$CaCO_3$ pretreated with MPTMS. The coupling of MPTMS and grafting of PMMA onto $CaCO_3$ were confirmed by IR spectrum. The grafting efficiency of PMMA was much higher in case of using MPTMS pretreated $CaCO_3$ than in case of using stearic acid pretreated $CaCO_3$.

Table 1 Influence of the modifier type and $CaCO_3$/MMA ratio on the polymerization conversion, f_r and f_e

Sample	Modifier type	$CaCO_3$/MMA	Conversion (%)	f_r (%)	f_e (%)
1	Stearic acid	2/3	85	2.86	2.38
2	MPTMS	2/3	81	14.25	12.42
3	MPTMS	1/2	89	18.69	11.12
4	MPTMS	1/3	93	22.46	8.53



(a) (b)

Fig.5 TEM micrographs of original $CaCO_3$ (a) and PMMA/$CaCO_3$ (b) composite prepared by emulsion polymerization

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