Colloid Polym Sci (2004) 282: 1374–1380
DOI 10.1007/s00396-004-1064-9

ORIGINAL CONTRIBUTION

Long Jiang
Yi Dan

Preparation of poly(methyl methacrylate)/$CaCO_3$/SiO_2 composite particles via emulsion polymerization

Received: 3 October 2003
Accepted: 6 December 2003
Published online: 4 March 2004

L. Jiang · Y. Dan (✉)
The State Key Laboratory of Polymer Materials Engineering,
Polymer Research Institute,
Sichuan University,
610065 Chengdu, China
E-mail: yqchen@email.scu.edu.cn
Tel.: +86-28-85407286
Fax: +86-28-85402465

Abstract A novel method to prepare organic/inorganic composite particles, i.e. poly(methyl methacrylate)/$CaCO_3$/SiO_2 three-component composite particles, using emulsion polymerization of methyl methacrylate with sodium lauryl sulfate as a surfactant in an aqueous medium was reported. $CaCO_3$/SiO_2 two-component inorganic composite particles were obtained firstly by the reaction between Na_2CO_3 and $CaCl_2$ in porous silica (submicrometer size) aqueous sol and the specific surface area of the particles was measured by the Brunauer–Emmett–Teller (BET) method. The results show that the BET specific surface area of the $CaCO_3$/SiO_2 composite particle is much smaller than that of the silica particle, indicating that $CaCO_3$ particles were adsorbed by porous silica and that two-component inorganic composite particles were formed. Before copolymerization with methyl methacrylate, the inorganic composite particles were coated with a modifying agent through covalent attachment. The chemical structures of the poly(methyl methacrylate)/$CaCO_3$/SiO_2 composite particles obtained were characterized by Fourier transform IR spectroscopy and thermogravimetric analysis. The results show that the surface of the modified inorganic particles is grafted by the methyl methacrylate molecules and that the grafting percentage is about 15.2%.

Keywords Emulsion polymerization · $CaCO_3$/SiO_2composite particle · Poly(methyl methacrylate) · Polymer/inorganic composite particles

Introduction

Owing to their extraordinary properties derived from the synergism between the properties of the components, polymer/inorganic composite materials offer very interesting actual and potential application. For instance, a composite from polypyrrole derivatives and tin dioxide can be used as a chemical sensor for the quantitative detection of the target organic vapors because of its reversible changes in electrical resistance at room temperature when exposed to a variety of different organic vapors, such as esters, alcohols and ketones [1]. Polymer/silica glass composite particles can be used as optically transparent materials because of their low optical losses and high optical quality [2]. Polymer encapsulated TiO_2 particles can obviously increase the stability and gloss of coatings [3]. Polymer-encapsulated inorganic particles may also have interesting applications in areas such as magnetics, adhesives, paint and electronics [4].

There are several routes to these polymer/inorganic composite materials, but emulsion polymerization may be one of the most effective methods. Owing to its advantages, such as high reaction rate, good heat dispersion and relatively sophisticated engineering technology in industry, emulsion polymerization has attracted extensive interest. Hasegawa et al. [5, 6] studied the free emulsion polymerization of methyl methacrylate (MMA) in an aqueous medium in the presence of a series of inorganic particles, such as calcium carbonate and titanium dioxide, and obtained composite particles with an inorganic particle core and a poly(methyl methacrylate) (PMMA) shell. Bourgeat-Lami and Lang [7, 8] prepared polystyrene beads containing silica particles by dispersion polymerization in polar media. Wang et al. [9] obtained the long-term stable poly(butyl acrylate) latex containing nanosilica through ultrasonic induced encapsulating emulsion polymerization. In our group, a series of systematic studies on the preparation of polymer/inorganic composite particles via emulsion polymerization are proceeding, including the method to graft PMMA onto the surface of silica particles and the influence of factors of the polymerization. Some of the work has been reported [10, 11].

According to the literature, polymer/inorganic composite particles have attracted more and more attention and there are still some problems to be solved, which can be summarized as follows:

1. In regard to some inorganic particles, such as $CaCO_3$, the surface of which is chemical inert or poorly active toward modifying agents, it is difficult to encapsulate them by a polymer layer through covalent attachment.
2. Most of the reported work focused only on composites between a single kind of inorganic particle and a single kind of polymer, resulting in poor synergistic properties arising from polymer and inorganic materials.

To avoid these drawbacks and to use our previous work as a base [10, 11] we present a new way to prepare polymer/inorganic composite particles through combining the polymer/inorganic composite technique with the inorganic/inorganic composite technique. The difference between this method and the other methods mentioned earlier is the presence of another inorganic particle. This inorganic particle is porous and easy to react with modifying agents such as silane coupling agents. Before polymerization, the chemically inert inorganic particles were firstly adsorbed by the active porous inorganic particles to prepare the two-component inorganic composite particles. Then, these inorganic composite particles were pretreated with modifying agent. Finally, through copolymerizing the modified inorganic composite particles with the organic molecules, the three-component polymer/inorganic composite particles could be obtained.

The PMMA/$CaCO_3$/SiO_2 system was chosen as a model to investigate the methods of obtaining polymer/inorganic part 1/inorganic part 2 three-component composite particles, in which the polymer part and the inorganic part were attached by a covalent bond through emulsion polymerization. The specific surface area, the average pore size and the average pore volume of $CaCO_3$ particles, SiO_2 particles and $CaCO_3$/SiO_2 composite particles were measured by the Brunauer–Emmett–Teller (BET) method and the results illustrate that $CaCO_3$ particles are adsorbed by porous SiO_2 particles. The structure and the grafting percentage were characterized by means of Fourier transform (FT) IR spectroscopy and thermogravimetric analysis (TGA). The results indicate that PMMA/$CaCO_3$/SiO_2 three-component composite particles were obtained and that the grafting percentage is about 15.2%.

Experimental

Materials

The MMA, provided by Rongfeng Chemical Factory (Chengdu, China), was further purified by distillation at a reduced pressure. The silica particles with a specific surface area of about 220 $m^2\ g^{-1}$ were supplied by Shengyang Chemical Reagent Factory (Shengyang, China). Na_2CO_3 and $CaCl_2$ were commercial products and were used without further purification. The modifying agent from Ha'erbin Chemical Research Institute (Ha'erbin, China), was analytical reagent grade and was used without further purification. The sodium lauryl sulfate (SLS) and the potassium persulfate (KPS) were purchased from Wuhan Chemical Reagent Factory (Wuhan, China). The chloroform and the ethanol used in this work were available commercially. Water was deionized before use.

Preparation of $CaCO_3$/SiO_2 two-component composite particles

The $CaCO_3$/SiO_2 two-component composite particles were prepared as follows. The silica particles (60 g) were place in a round-bottom flask containing 300 g deionized water. To this suspension were added Na_2CO_3 aqueous solution (500 ml, 2 mol l^{-1}) and $CaCl_2$ aqueous solution (200 ml, 5 mol l^{-1}). After reaction of this system under mechanical stirring at 50 °C for 4 h, the resulting solid was washed several times with deionized water to remove the NaCl produced. Then it was dried at 80 °C and crushed with a mortar to afford the $CaCO_3$/SiO_2 two-component composite particles.

Modification of the $CaCO_3$/SiO_2 two-component composite particles

Before polymerization, the $CaCO_3$/SiO_2 composite particles were modified in modifying agent ethanol solution and dried at 60 °C to remove ethanol. The amount of modifying agent used to modify the $CaCO_3$/SiO_2 composite particles was 5% of that of the amount of $CaCO_3$/SiO_2 composite particles.

Preparation of the PMMA particles

The PMMA particles were obtained through emulsion polymerization of MMA. Firstly, purified MMA (20 g), SLS (6 g) and deionized water (60 g) were placed in a three-neck bottle with a thermometer, a stirrer and a refluxing condensation pipe to prepare the MMA emulsion. Then, to this emulsion was added KPS aqueous solution and the polymerization was carried out at 80 °C for about 3 h. After being coagulated with the $CaCl_2$ aqueous solution, the PMMA latex was filtered, washed with water to demulsify it, dried at 60 °C and pulverized to get PMMA particles.

Preparation of the PMMA/$CaCO_3$/SiO_2 three-component composite particles

PMMA/$CaCO_3$/SiO_2 three-component composite particles were prepared through grafting emulsion polymerization of MMA onto the surface of $CaCO_3$/SiO_2 composite particles. Firstly, the SLS aqueous solution and the modified $CaCO_3$/SiO_2 composite particles were charged successively in a three-neck bottle under mechanical stirring. After 20 min, to this suspension were added purified MMA monomer and KPS aqueous solution. Then, emulsion polymerization was carried out at 80 °C for about 4 h. After cooling, the PMMA/$CaCO_3$/SiO_2 three-component composite particles obtained were precipitated with the water solution of $CaCl_2$, then the precipitation was filtered, washed with deionized water to remove emulsifier, dried and crushed. After that the PMMA/$CaCO_3$/SiO_2 three-component composite particles were obtained.

Preparation of the mixture of the PMMA particles with the modified $CaCO_3$/SiO_2 composite particles

By blending the PMMA particles with modified $CaCO_3$/SiO_2 composite particles at a 1:1 mass ratio of PMMA to $CaCO_3$/SiO_2 at ambient temperature directly, the mixture was obtained.

Characterization

Determination of specific surface area

The specific surface areas of silica particles, calcium carbonate particles and $CaCO_3$/SiO_2 composite particles were determined by the BET method. All the samples were analyzed using a ZXF-05 automatic adsorption instrument designed by Northwest Chemical Research Institute.

FTIR measurement

The chemical structures of all the samples were determined using a Nicolet 560 FTIR spectrometer. Before the FTIR measurement, both the PMMA/$CaCO_3$/SiO_2 three-component composite particles and the mixture of the PMMA particles with the modified $CaCO_3$/SiO_2 composite particles were extracted with chloroform for 7 days in a Soxhlet extractor, and dried at 60 °C to remove the solvent. Then, the samples of $CaCO_3$ particles, the $CaCO_3$/SiO_2 composite particles, the PMMA/$CaCO_3$/SiO_2 three-component composite particles and the mixture of PMMA with $CaCO_3$/SiO_2 composite particles for characterization were pretreated in the form of KBr pellets.

TGA measurement

TGA of PMMA/$CaCO_3$/SiO_2 three-component composite particles was performed with a Dupond 2100 thermal analysis instrument. The samples were heated over the temperature range 25–600 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere, and the nitrogen flow rate was 50 ml min^{-1}.

Determination of the grafting percentage

The grafting percentage was defined as the mass percentage of polymer grafted onto inorganic particles based on the total inorganic particles used, and was determined by the following equation [12]:

$$\text{Percentage of grafting (G\%)} = \frac{\text{polymer grafted (g)}}{CaCO_3/SiO_2 \text{ used (g)}} \times 100\%, \tag{1}$$

where the mass of polymer grafted and $CaCO_3$/SiO_2 used were determined by the results of TGA measurement of PMMA/$CaCO_3$/SiO_2 three-component composite particles.

Determination of the grafting efficiency

The grafting efficiency was defined as the mass percentage of PMMA grafted on $CaCO_3$/SiO_2 composite particles, based on the total PMMA, and was determined by the following equation:

$$\text{Grafting efficiency (E\%)} = \frac{CaCO_3/SiO_2 \text{ used} \times \text{percentage of grafting}}{\text{MMA used} \times \text{conversion of MMA}} \times 100\%. \tag{2}$$

Determination of the conversion of MMA

The conversion of MMA (C%) was determined by means of the gravity method and was calculated using the following equation:

$$C\% = \frac{M_2 - M_1 Y - M_3}{M_1 X} \times 100\%, \tag{3}$$

where M_1 is the mass of the polymerized emulsion sample, M_2 is the mass of the solid after drying, M_3 is the mass of the inhibitor, X is the mass percentage of MMA based on total input materials and Y is the mass percentage of SLS, KPS and SiO_2 based on total input materials.

Results and discussion

Specific surface area of the $CaCO_3$/SiO_2 inorganic composite particles

Before polymerization, the $CaCO_3$ particles were adsorbed by porous SiO_2 particles and the process of this adsorption is described in Fig. 1.

As we know that the surface area of porous material is mainly from the internal surface area, and if the pores are full of other particles, the internal surface will decrease greatly. Hence, the silica specific surface area and the average pore volume will decrease if the $CaCO_3$particles obtained really come into the pores.

The specific surface area and the average pore volume were measured by the BET method and the data are listed in Table 1. From Table 1, it can be seen that the BET specific surface area of the $CaCO_3$/SiO_2 composite particles is 36.5 m^2 g^{-1}, much smaller than that of the silica (223.6 m^2 g^{-1}) and that of the mixture (81.8 m^2 g^{-1}) of $CaCO_3$ particles with SiO_2 particles

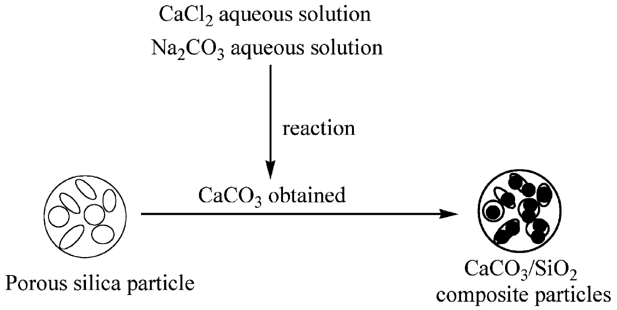

Fig. 1 Schematic diagram of the $CaCO_3/SiO_2$ composite particle preparation

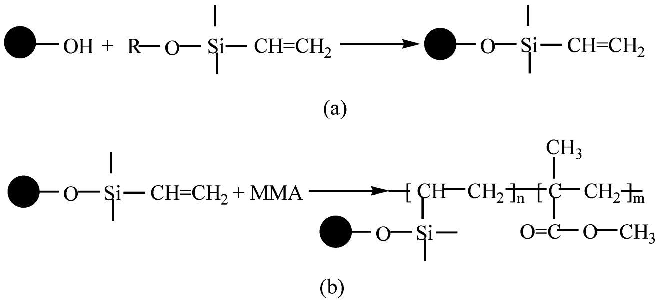

Fig. 2 Schematic diagrams of **a** modification of $CaCO_3/SiO_2$ composite particles and **b** grafting of methyl methacrylate onto the surface of $CaCO_3/SiO_2$ composite particles

Table 1 Results of the Brunauer–Emmett–Teller (*BET*) measurement of the particles

Samples	BET specific surface area ($m^2\ g^{-1}$)	Average pore volume ($cm^3\ g^{-1}$)
SiO_2particle	223.6	0.42
$CaCO_3$particle	3.4	0.01
$CaCO_3/SiO_2$ composite particle[a]	36.5	0.09
Mixture of $CaCO_3$ with SiO_2[b]	81.8	0.18

[a]The mass ratio of $CaCO_3$particles to SiO_2 particles is 1:1
[b]The mixture of $CaCO_3$ with SiO_2 at 1:1 mass ratio of $CaCO_3$ to SiO_2

Table 2 Mass loss of the mixture and composite particles. Poly(methyl methacrylate) (*PMMA*)

Samples	Mass loss (mass%)	Remaining PMMA (mass%)
Mixture of PMMA with $CaCO_3/SiO_2$	53.4	0
PMMA/$CaCO_3/SiO_2$ composite particle	43.1	6.9

with 1:1 mass ratio of $CaCO_3$ to SiO_2. This indicates that, for the $CaCO_3/SiO_2$ composite particles, a lot of pores of SiO_2 particles are full of $CaCO_3$ particles. The large decrease of the average pore volume of the SiO_2 particles after adsorption also confirms this conclusion. So the $CaCO_3/SiO_2$ composite particles were obtained.

Prior to copolymerization with MMA, the $CaCO_3/SiO_2$ composite particles were modified in modifying agent ethanol solution. The modifying agent has silanol groups which can react with hydroxyl groups on the surface of $CaCO_3/SiO_2$ composite particles, and vinyl groups which can react with MMA in the copolymerization (Fig. 2). From Fig. 2, it can be inferred that the PMMA/$CaCO_3/SiO_2$ three-component composite particles, in which the polymer part and the inorganic part are attached by a covalent bond, should be obtained. In order to confirm this inference, two samples were employed. One was the mixture of PMMA particles with $CaCO_3/SiO_2$ two-component composite particles, and the other was the PMMA/$CaCO_3/SiO_2$ three-component composite particles. In the first case, the mass ratio of PMMA particles to $CaCO_3/SiO_2$ two-component composite particles was 1:1, which is as same as that of MMA to $CaCO_3/SiO_2$ in the recipe for the synthesis of the PMMA/$CaCO_3/SiO_2$ three-component composite particles. These two samples were extracted by chloroform under the same conditions. The mass loss of these samples after extraction is shown in Table 2. From the table we can see that the mass loss of the mixture is 53.4%, indicating that all of the PMMA particles have been extracted. The mass loss of the composite particles, however, is only 43.1%, and this illustrates that about 6.9% PMMA still existed in the composite particles. The unextracted part of PMMA in the composite particles is supposed to graft onto the surface of $CaCO_3/SiO_2$ particles. In order to prove this assumption, the extracted mixture of PMMA with $CaCO_3/SiO_2$ and the extracted PMMA/$CaCO_3/SiO_2$ three-component composite particles were measured further by FTIR spectroscopy.

The FTIR spectra of the mixture of PMMA with $CaCO_3/SiO_2$ and the PMMA/$CaCO_3/SiO_2$ three-component composite particles are shown in Figs. 3 and 4, respectively. In Fig. 3, the characteristic absorption band of Si–O at 1,097 cm^{-1} [13] and the characteristic absorption band of CO_3^{2-} at 1,448 cm^{-1} [14] can be found, while the characteristic absorption band of carbonyl (C = O) in PMMA at about 1,730 cm^{-1} [15] cannot be found. In Fig. 4, however, all the characteristic absorption bands of Si–O at 1,099 cm^{-1}, of CO_3^{2-} at 1,420 cm^{-1} and of carbonyl in PMMA at 1,733 cm^{-1} can be found, indicating that the PMMA molecules were indeed grafted onto the surface of $CaCO_3/SiO_2$ composite particles. In addition, in the mixture of PMMA with $CaCO_3/SiO_2$ the mass ratio of PMMA polymer particles to $CaCO_3/SiO_2$ composite particles is the same as that of MMA monomer to $CaCO_3/SiO_2$ composite

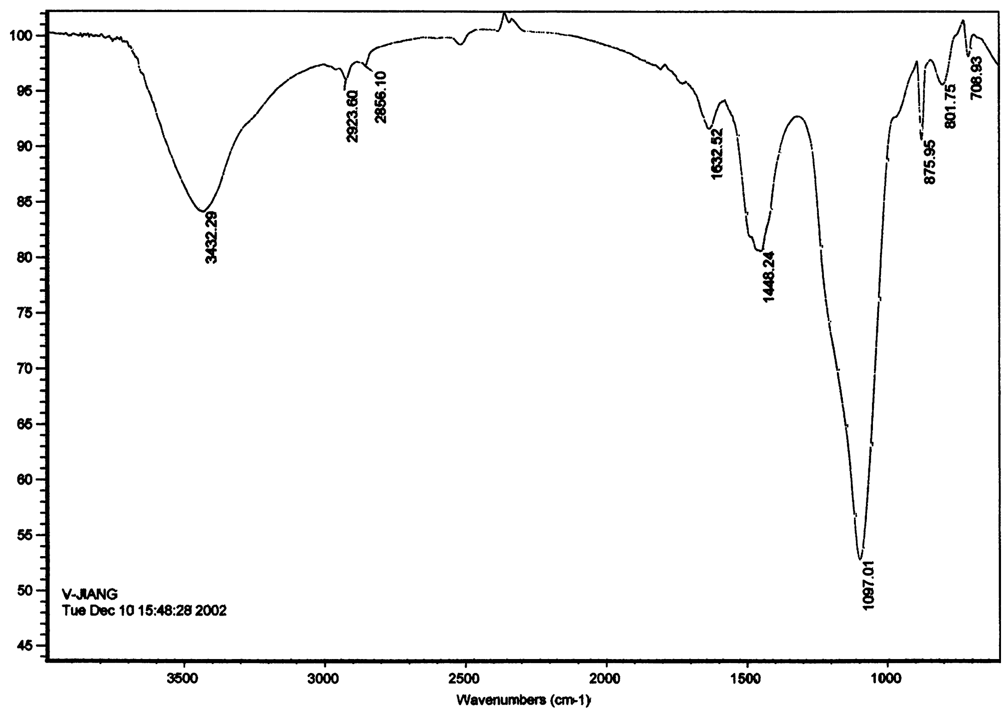

Fig. 3 Fourier transform (*FT*) IR spectrum of a mixture of poly(methyl methacrylate) (*PMMA*) with $CaCO_3/SiO_2$ composite particles

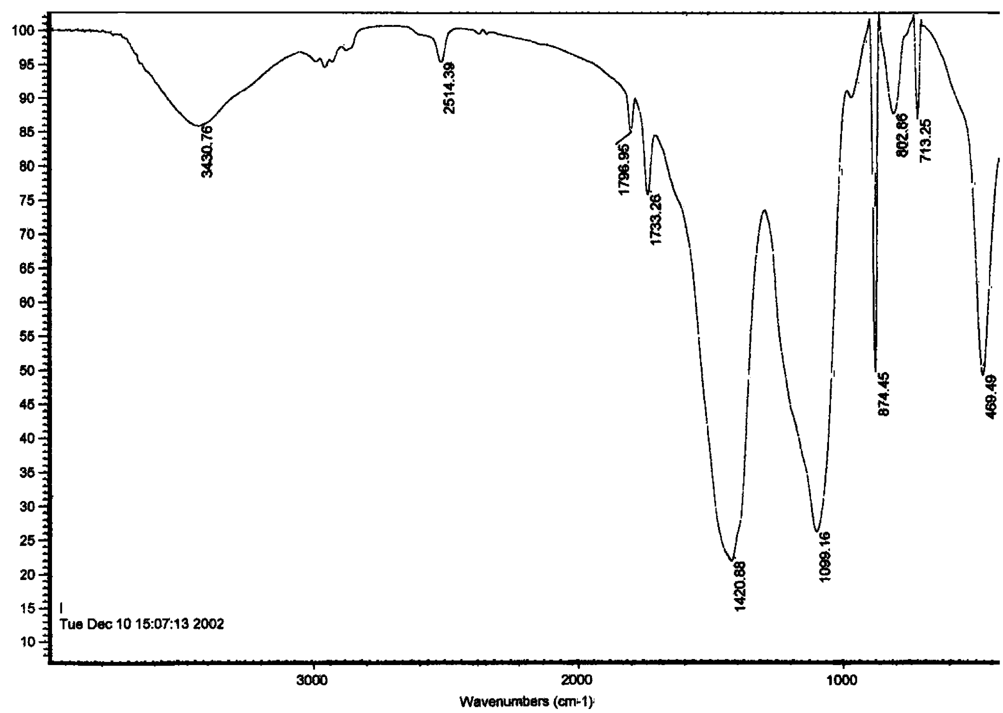

Fig. 4 FTIR spectrum of the PMMA/$CaCO_3/SiO_2$ three-component composite particles

particles in the recipe for the synthesis of PMMA/$CaCO_3/SiO_2$three-component composite particles, and both samples were extracted under the same conditions. For these reasons, the conclusion that the PMMA molecules are grafted onto the surface of $CaCO_3/SiO_2$ particles is justified.

The $CaCO_3$ particles which were used to prepare the PMMA/$CaCO_3/SiO_2$ composite particles mentioned earlier were adsorbed by SiO_2 particles before being modified. In order to investigate the influence of SiO_2 on the polymerization of MMA in the presence of $CaCO_3$/SiO_2 inorganic composite particles, the grafting poly-

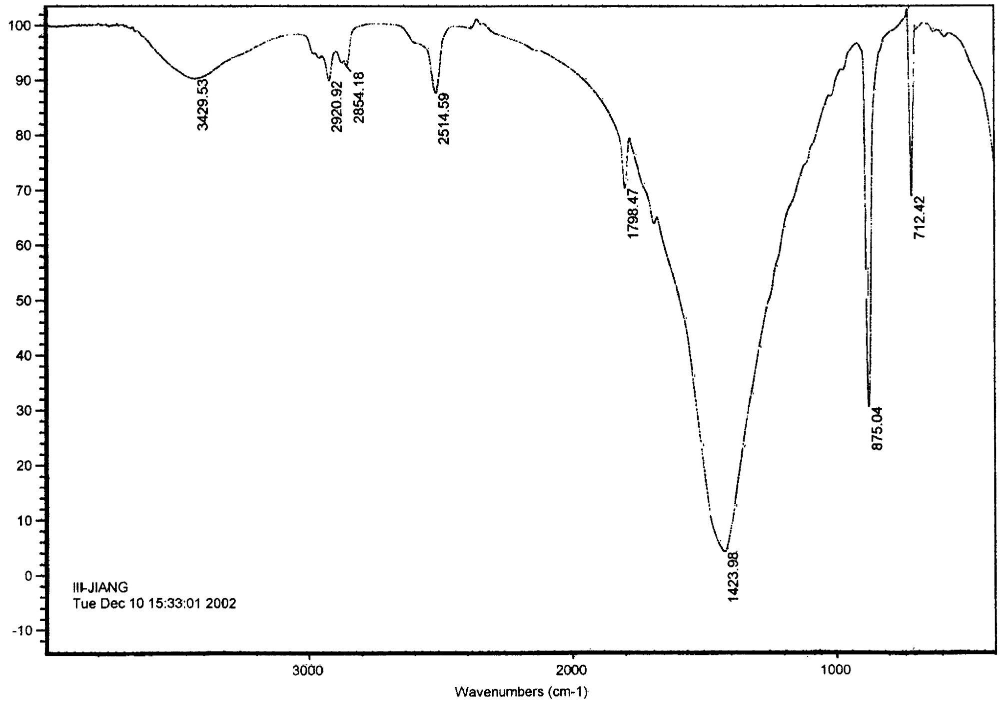

Fig. 5 FTIR spectrum of the PMMA/$CaCO_3$ composite particles

merization of PMMA onto the $CaCO_3$ surface was also studied. The $CaCO_3$ particles were pretreated the same as the $CaCO_3/SiO_2$ composite particles had been, and were copolymerized with MMA under the same conditions as mentioned previously. Then, the PMMA/$CaCO_3$ particles obtained were extracted with refluxing chloroform for 7 days, and the results show that almost all of the PMMA particles were removed. The FTIR spectrum of PMMA/$CaCO_3$ particles (Fig. 5) confirms this conclusion. The characteristic absorption band of carbonyl in PMMA at about 1,730 cm^{-1} cannot be found in this figure, which indicates that there are no strong interactions, such as covalent attachment, between the PMMA and the $CaCO_3$. It seems that the $CaCO_3$ particles were encapsulated with PMMA, and the interactions may be physical. Hence, PMMA molecules were removed by chloroform and the characteristic absorption band cannot be found. This may be the result of the chemically inert $CaCO_3$ surface and its poor reactivity on the modifying agent [16].

The conversion of MMA was determined by the gravimetric method, and the results were listed in Table 3. Samples 1–3 were all sampled from the same bottle of emulsion. From the table we can see that the conversion of MMA is about 96.72%. The PMMA obtained, however, should be formed not only on the surface of $CaCO_3/SiO_2$ composite particles but also in the aqueous medium. To determine the amount of PMMA grafted on the surface of $CaCO_3/SiO_2$ composite particles and that formed in the aqueous medium, the TGA measurement was used. Prior to TGA measurement, the

Table 3 Conversion of methyl methacrylate (*MMA*)

Sample	M_1 (g)	M_2 (g)	M_3 (g)	X (%)	Y (%)	C%
1	1.5396	0.5258	0.00788	0.1642	0.1790	95.9
2	1.7128	0.5894	0.00895	0.1642	0.1790	97.4
3	1.6771	0.5751	0.00794	0.1642	0.1790	96.9
Average conversion of MMA						96.7

* The meanings of M_1, M_2, M_3, X, Y and C% are the same as in Eq. 3, and C% is calculated according to Eq. 3

PMMA/$CaCO_3/SiO_2$ three-component composite particles were extracted with chloroform and all of the ungrafted PMMA molecules were removed. Hence, the loss mass and the remains of the sample during TGA measurement can substitute the mass of PMMA grafted and the mass of $CaCO_3/SiO_2$ composite particles in Eq. (1). The TGA curve of the PMMA/$CaCO_3/SiO_2$ composite particles is shown in Fig. 6. In this figure, the loss mass is 13.2%, which attests that the PMMA has grafted onto the $CaCO_3/SiO_2$ composite particles, and the percentage of the remains is 86.8%, so the grafting percentage is 15.2% according to Eq. (1). While the conversion of MMA was 96.7%, according to Eq. (2), the grafting efficiency can be calculated as 15.8%.

Conclusion

Through pretreating the $CaCO_3/SiO_2$ inorganic composite particles with modifying agents and emulsion

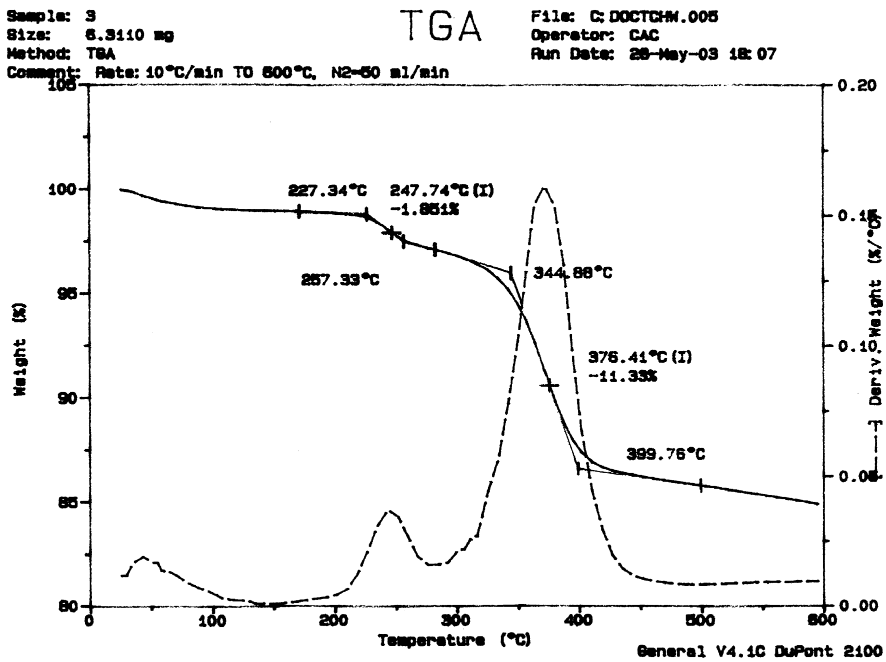

Fig. 6 Thermogravimetric analysis curve of the PMMA/$CaCO_3$/SiO_2 three-component composite particles

polymerization of MMA in the presence of the modified $CaCO_3$/SiO_2 composite particles, the PMMA molecules can be grafted onto the surface of inorganic particles, and PMMA/$CaCO_3$/SiO_2 three-component composite particles can be obtained. A novel method to prepare multicomponent polymer/inorganic composite particles with strong interaction (e.g. covalent interaction) between the polymers and the inorganic particles has been found. Through this method, many functional polymer/inorganic composite particles can be prepared.

Acknowledgements The authors are grateful to the National Natural Science Foundation of China (29974021, 20034006) and the National Educational Ministry of China for support of this research.

References

1. de LacyCostello BPJ, Evans P, Ewen RJ, Honeybourne CL, Ratckiffe NM (1996) J Mater Chem 6:289–294
2. Gvishi R, Narang U, Ruland G, Kumar DN, Prasad PN (1997) Appl Organomet Chem 11:107–127
3. Caris CCH, van Elven LPM, van Herk AM, German AL (1989) Br Polym J 2:133.
4. Jin LM, Chen YF, Zhang GC, Xie YS (1995) Funct Mater J 5:452–454
5. Hasegawa M, Arai K, Satio S (1982) J Polym Sci Part A Polym Chem 20:1021–1029
6. Hasegawa M, Arai K, Satio S (1987) J Polym Sci Part A Polym Chem 25:3231–3239
7. Bourgeat-Lami E, Lang J (1998) J Colloid Interface Sci 197:293–308
8. Bourgeat-Lami E, Lang J (1999) J Colloid Interface Sci 210:281–289
9. Wang Q, Xia HS, Zhang CH (2001) J Appl Polym Sci 80:478–1488
10. Yang Y, Dan Y (2002) IUPAC World Polymer Congress Preprints (II) 640
11. Yang Y, Dan Y (2002) Colloid Polym Sci
12. Tsubokawa N, Fujiki K, Sone Y (1988) Polym J 20:213–220
13. Silverstein RM, Bassler GC, Morrill TC (1982) Spectrometric identification of organic compounds. Science, Beijing, p 136
14. Liu YX (2001) Spectrometric identification. College of Chemical Engineering of Sichuan University, p 99
15. Silverstein RM, Bassler GC, Morrill TC (1982) Spectrometric identification of organic compounds. Science, Beijing, p 91
16. Nakatsuka T, Kawasaki H, Itadani K, Yamashita S (1981) J Colloid Interface Sci 82:298