An effective approach to synthesis of poly(methyl methacrylate)/silica nanocomposites

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Abstract
A novel synthetic route for nearly monodispersed poly(methyl methacrylate)/SiO$_2$ composite particles (PMSCP) is reported. Silica nanoparticles modified with oleic acid were used as 'seeds'. Methyl methacrylate (MMA) monomer was copolymerized with oleic acid via *in situ* emulsion polymerization, in the presence of an initiator; it resulted finally in the formation of composites with core–shell morphology. The composite particles were examined by transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The number of silica particles inside the composite particles increases with an increase in the silica concentration. The effect of grafted silica concentration on the morphology of PMSCP is also reported in detail. It was found by thermogravimetric analysis that PMSCP show a potential application for fire retardance.

1. Introduction

Encapsulation technologies are becoming more and more popular, since polymer-encapsulated particles can offer very interesting actual and potential applications. The incorporation of inorganic materials on the nanoscale can enhance fire retardancy [1, 2] and mechanical strength [3–5] of organic polymers and coatings. In the past few years, there has been increasing interest in the synthesis of particulate or colloidal polymer encapsulation, which has shown various applications, such as nanolithography [6, 7], solid polymer electrolytes [8], etc.

Owing to the many uses of silica [9–11], different methods for the synthesis of polymer–silica particles have been reported. Previous preparations have mostly involved soaking techniques (dipping a polymer film into the perhydropolysilazane solution) [12], reverse w/o microemulsion polymerization [13], and a sol–gel process [14–16]. In addition,

the surfactant-free synthesis of PMMA/silica nanocomposite particles has been achieved in aqueous alcoholic media at ambient temperature without the use of auxiliary comonomers [17]. In those related works, vinyl polymer–silica nanocomposite particles were synthesized [18–20]. Chen *et al* reported the synthesis of raspberry-like PMMA/SiO$_2$ nanocomposite particles via a free-radical copolymerization of methyl methacrylate (MMA) with 1-vinylimidazole in the presence of ultrafine aqueous silica sols [21, 22]. Most of those previous reports were related to the poly(methyl methacrylate)/silica hybrid materials. As we know, the compatibility between inorganic particles and polymer is not good in these materials, which further restricts the application of hybrid materials. As in our early report, it has been found poly(methyl methacrylate)/SiO$_2$ composite particles show excellent compatibility between inorganic particles and polymer without any obvious interface. Until now, only a few works have been reported on the synthesis of poly(methyl methacrylate)/SiO$_2$ composite particles. Pu [4],

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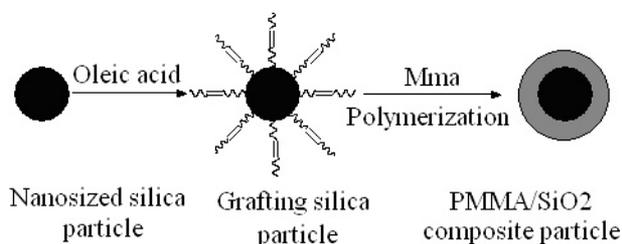
Scheme 1. Schematic illustration of the PMSCP synthesis process.

Zhang [23], Luna-Xavier [24] and their coworkers had described a preparation of poly(methyl methacrylate)/SiO$_2$ composite particles. Their works focused on the methods of grafting 3-(trimethoxysilyl) propyl methacrylate (MPS), and using a cationic initiator (AIBA). The key point, in these previous works, is that the mineral surface must be modified by chemical bonding or specific adsorption to trigger subsequent coatings. Thus a specific interaction between the silica particles and the polymer is essential for nanocomposite formation. Following this line, we select oleic acid as a modified monomer. In this paper, the idea of oleic acid-functionalized silica nanoparticles for subsequent PMMA coating is been reported.

In our previous work [25], we synthesized polystyrene/SiO$_2$ composite particles (PSCP). In the present work, we report new results on the synthesis of PMSCP via *in situ* emulsion polymerization. This includes three distinct stages. First, monodisperse silica particles with controlled diameters were obtained by the Stöber's method [26] using tetraethyl orthosilicate (TEOS) and ammonia as materials. The second stage was crucial and involved the chemisorption of oleic acid [27], which was expected to react with the growing polymethyl methacryl radicals and thus promoted anchoring of the polymer chains on the silica surface. Finally, the surface-modified silica nanoparticles were then used in the encapsulation process. MMA monomer was copolymerized with oleic acid via *in situ* emulsion polymerization, in the presence of an initiator. Scheme 1 illustrates the synthesis process of PMSCP. PMSCP was finally obtained through polymerization of MMA monomer on the surface of grafted silica nanoparticles. The effect of the amount of grafted silica on the particle size and size distribution is also reported in the following part. Moreover, it is worth noticing that the resulting PMSCP has uniform size and high yields.

2. Experimental section

2.1. Materials

Absolute ethanol, distilled water, methyl methacrylate (MMA), potassium persulfate (KPS), oleic acid, polyoxyethylene octylphenyl ether (OP), ammonia, sodium dodecyl sulphonate (DBS), sodium bicarbonate (NaHCO$_3$), and TEOS are analytical grade and used as received.

2.2. Preparation for stable dispersions of oleic-acid-modified nanosized silica

We synthesized small silica nanoparticles (<100 nm) using TEOS as material under alkaline conditions in an ethanol
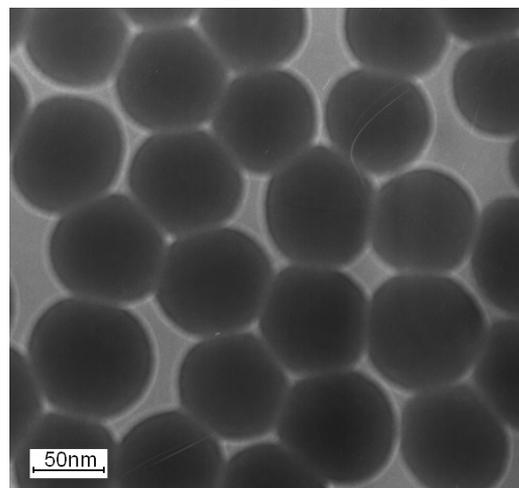

Figure 1. TEM image of grafted silica particles with average diameter of 80 nm.

medium, as introduced by Stöber. Then, silica nanoparticles were grafted to oleic acid. The synthesis follows the procedures as in our previous report [25]. Figure 1 shows a TEM image of grafted silica particles with an average diameter of 80 nm. Also, a uniform size and narrow size distribution can be observed. The amount of oleic acid has been determined from the thermogravimetric analysis (TGA) curve of grafted silica particles with a TGA/SDTA851^e analyser at a heating rate of 10 °C min^{-1} from 50–800 °C under a nitrogen flow. The content of oleic acid in grafted silica was estimated to be about 4.47%.

2.3. Preparation for PMSCP via in situ emulsion polymerization

A series of encapsulation experiments was carried out in a 500 ml four-neck flask equipped with a condenser. The reaction vessel was purged with nitrogen to remove all traces of oxygen. In a typical polymerization, the required amount of surfactant (OP:DBS = 1:1) and sodium bicarbonate were dissolved under a nitrogen atmosphere in distilled water in a round-bottom flask. MMA and the modified silica were added quantitatively into the pre-emulsion, individually. The grafted silica was dispersed into absolute ethanol by ultrasonication before it was added into the reactor. Then, potassium persulfate was added into the reactor. Subsequently, this emulsion was heated under mechanical stirring up to 50 °C. The MMA monomer was copolymerized with oleic acid on the surface of grafted silica nanoparticles in the presence of an initiator. The reaction went on for 30 h at 50 °C in a nitrogen atmosphere. Finally, the emulsion of PMSCP without any post-preparative treatment was obtained.

2.4. Characterizations

The morphology of the PMSCP was investigated by transmission electron microscopy (TEM) (JEOL 2000EX) at an accelerator voltage of 200 kV. TGA of the PMSCP was performed on a TGA/SDTA851^e analyser at a heating rate of 10 °C min^{-1} from 50 to 800 °C under a nitrogen flow.
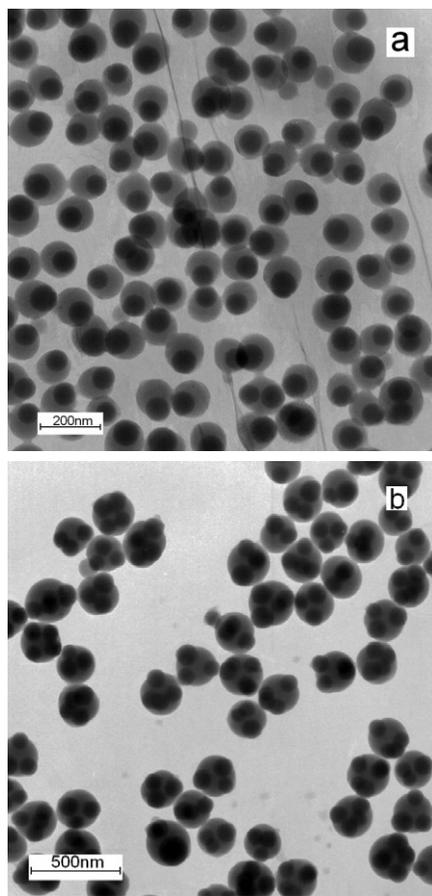
Figure 2. TEM images of PMSCP. The amount of grafted silica is (a) 0.5 g (S-1 in table 1) and (b) 2.0 g (S-4 in table 1). The amount of MMA is 10.0 ml.

The size and size distribution of PMSCP were determined by scanning electron microscopy (SEM) (JEOS JSM-5600) and a dynamic light scattering (DLS) instrument (Zetasizer 3000HSA MALVERN). For TEM, the emulsion was dispersed in pure water, dropped on a copper grid, and then irradiated with an infrared (IR) trip lamp. X-ray photoelectron spectra (XPS) (ESCALAB Mark II) were recorded to examine the component on the surface of PMSCP. Infrared spectra of the samples as power-pressed KBr pellets were collected in the range from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1} on a Nicolet AVATAR360 Fourier transform infrared (FTIR) spectrometer.

3. Results and discussions

Figure 2 shows TEM images of samples S-1 and S-4 prepared as described in table 1. All the images show that silica nanoparticles are embedded inside the PMMA and no free silica particles are outside. Moreover, some changes in the particle size and morphology, as well as in the number of silica particles per composite particle, are observed when the amount of the silica particles was changed from 0.5 to 5 g, as shown in figure 2 and in table 1. Figure 2(a) shows a TEM image of PMSCP. The morphology of the particles shows a good core–shell structure. PMMA shells coat the grafted silica
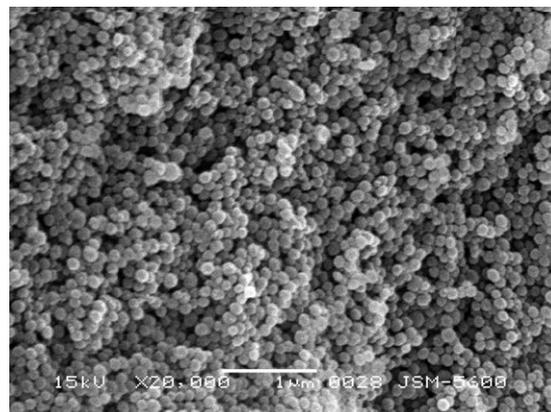
Figure 3. SEM image of PMSCP (S-1 in table 1).

Table 1. Characteristics of silica encapsulated by *in situ* polymerization of MMA monomer (the size and size distribution of PMSCP were determined using a dynamic light scattering (DLS) instrument).

Sample	Grafted silica/ MMA ratio (g:ml)	Diameter of composite particle (nm)
S-1	0.5:10	130
S-2	1:10	170
S-3	1.5:10	220
S-4	2:10	250
S-5	3:10	380
S-6	5:10	420

core nanoparticles, and the average diameters of the core–shell particles are about 120 nm. Also, approximately 97% of these core–shell particles have only one single core. The resulting PMSCP has high yields through using oleic acid as a functionalized monomer. After the polymerization process, the polymer that is formed was attached to the silica surface. So, the encapsulation of inorganic particles by polymers through polymerization is an effective way to prevent them from agglomeration. In this work, no other reaction conditions are changed, but the amount of grafted silica is increased in the reaction system (the result is shown in figure 2(b)). From the TEM image, it can be found distinctly that the average diameter of the composite particles was about 240 nm. Also, these numerous composite particles had three cores in figure 2(b) when the amount of grafted silica was 2.0 g in this reaction system. It can be considered that the MMA monomer was polymerized on the surface of the grafted silica when the polymerization was at an initial stage. MMA monomer gradually decreased as the polymerization reaction proceeded. The grafted silica nanoparticles were so excessive that they could not obtain enough MMA monomer in the middle stage of the reaction. Then, the grafted silica nanoparticles were 'hungry'. So, two, three, or many more silica particles shared the MMA monomer to maintain a balanced state of the reaction system.

PMSCP has been characterized further by SEM analysis (as shown in figure 3). As seen in figure 3, PMSCP is spherical and show a narrow size distribution. The distribution of the PMSCP takes a branched shape. A large number of spheres have an average diameter of about 120 nm and a smooth
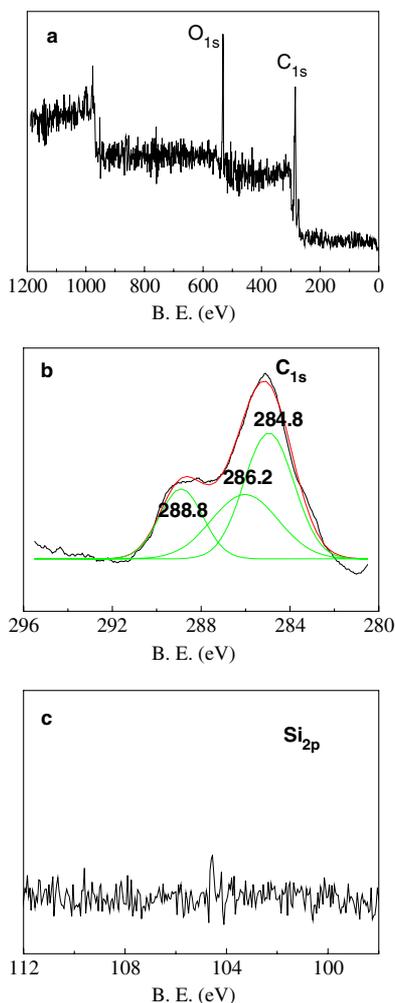
Figure 4. XPS spectra of PMSCP: (a) typical survey of PMSCP; (b) close-up survey at C_{1s}; and (c) close-up survey at Si_{2p}.
(This figure is in colour only in the electronic version)

Figure 5. The infrared spectra (range 4000–500 cm^{-1}) of (a) pure oleic acid, (b) PMSCP (sample S-4, table 1), and (c) PMMA.

Figure 6. DTG curves of PMMA (a), PMSCP (b, S-4), and PMSCP (c, S-6) at a heating rate of 10 °C min^{-1} under the nitrogen flow.

surface. Table 1 lists the resulting diameters of composite particles prepared at different ratios of grafted silica/MMA (g:ml). The average diameter of PMSCP was determined by dynamic light scattering analysis. The results indicate that it becomes bigger while the amount of grafted silica is increasing in the pre-emulsion, which is quite close to our TEM measurements. In addition, it is found that oleic acid plays an important role in interacting with the polymer.

X-ray photoelectron spectroscopy (XPS) is known to be a powerful method for investigating the core–shell particles, and it can provide more information concerning the chemical composition on the extreme surface (of a depth of about 5 nm). The C_{1s} and O_{1s} XPS spectrum of the composite particles is shown in figure 4(a). Since there are a large number –CH_2– groups in the nanocomposites, the binding energy of C_{1s} in a long alkyl chain can be used as a reference. The C_{1s} spectrum (in figure 4(b)) consists of peaks at 284.8, 286.2 and 288.8 eV, corresponding to C–C, C–H, C–O and C=O in alkyl and carboxylate carbon, respectively. According to the results of TEM, it can be concluded that silicon dioxide particles are included in PMSCP. As we know, the Si_{2p} peak is at 103.3 eV.
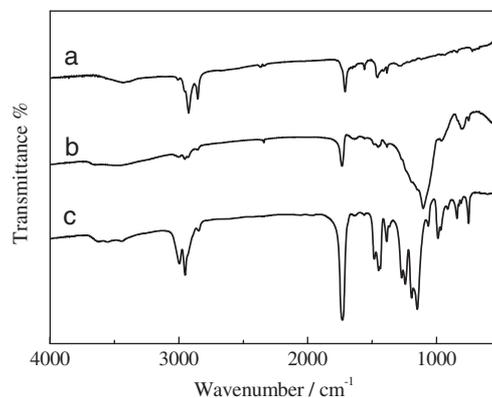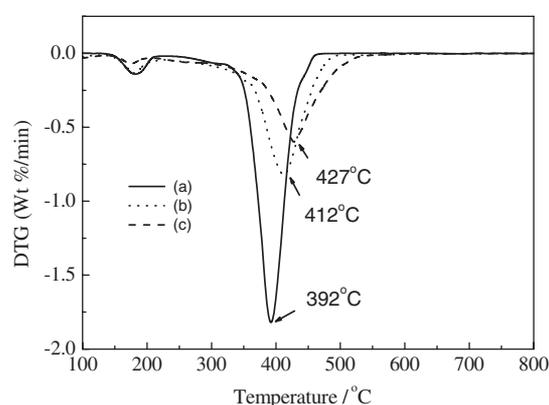
Figure 4(c) shows a close-up survey of Si_{2p}; there is no Si_{2p} peak in figure 4(c). These results illustrate that the PMSCP has an organic surface layer without any covered silica, confirming that PMSCP has high encapsulation yields.

Figure 5 shows the infrared spectra (range 4000–500 cm^{-1}) of pure oleic acid, PMMA, and PMSCP. The spectrum of pure oleic acid is shown in figure 5(a). There are three main features: CH_2 stretching bands at 2858 and 2925 cm^{-1}, and the C=O vibration at 1708 cm^{-1}. The spectra of PMMA and PMSCP are shown in figures 5(b) and (c). Comparing the IR spectra of PMMA and PMSCP with the PMMA standard, the strong IR absorption bands of PMMA at 3000, ∼1733, 1200–1170, and 960 cm^{-1} are in good agreement with the PMMA standard. The spectra of PMSCP (figure 5(b)) have quite different relative intensities to the corresponding CH_2 bands of a pure PMMA, and also displays a shift of the C=O band from 1708 to 1733 cm^{-1} due to the formation of hydrogen bonds between the carbonyl groups of the oleic acid and the silanol groups of silica. The absorption at 1106 cm^{-1} (Si–O–C) also confirms that the silica nanoparticles have been encapsulated well into the polymer. The results indicate that oleic acid bonded to a silica surface with either a single hydrogen bond or MMA monomer is polymerized successfully on the surface of grafted silica particles.

Figure 6 shows the DTG curves of the pure PMMA and PMSCP under a nitrogen flow at a heating rate of 10 °C min^{-1}.

It displays two main inflection regions. The first region at lower temperatures ($<200\,°C$) originates from the loss of absorption water and ethanol, while the region at higher temperature (350–$450\,°C$) is associated with the decomposition of PMMA. The residue of PMMA is 0.75%, while the residue of PMSCP is 23% (S-4, table 1) and 53% (S-6, table 1), respectively. As seen from the DTG curves, the maximum temperatures of weight loss (T_m) of PMMA and PMSCP (b, S-4; c, S-6) are 392, 412 and $427\,°C$, respectively. The results reveal that SiO_2 retards the thermal decomposition of the polymer chain. The T_m value of the PMSCP is independent of the silica content. The T_m value of the PMSCP increases with increasing silica content. This result may be ascribed to the uncondensed residual $Si(OH)_4$. In this work, the SiO_2 particles were derived from the hydrolysis and polycondensation of TEOS. The uncondensed residual $Si(OH)_4$ particles tend to decompose into SiO_2 and H_2O at a higher temperature. This process absorbs a large quantity of heat, and the H_2O can decrease the internal temperature of composite particles. So, it can retard the thermal decomposition of the polymer and make the T_m value increase. Moreover, the T_m value of composites is of the order PMMA $<$ S-4 $<$ S-6, suggesting that the silica content affects the property of the PMMA in the composites.

4. Conclusions

Here, we developed an easier and more effective method for preparing nearly monodispersed PMMA/SiO_2 composite particles. A strong interaction between the polymer and the silica particles is a prerequisite for the composite formation. In summary, the results provide us with a new method for an alternative synthetic strategy to fabricate novel materials and also provides further understanding of the formation mechanism of composite materials. Similarly, it could be possible and helpful to prepare other core–shell particles, for example, with ZnS, CdS, Fe_3O_4, TiO_2 and any other rare earths as core, which could be obtained only by simply modifying the surface with a coupling reagent.

Acknowledgments

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