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SHORT COMMUNICATION

Synthesis of polystyrene/SiO_2 composite microparticles by dispersion polymerization in supercritical fluid

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Abstract A novel synthetic route to prepare polystyrene/SiO_2 composite microparticles in supercritical carbon dioxide ($scCO_2$) is presented. Silica particles with the size of 130 nm which were surface-modified with 3-(trimethoxysilyl) propyl methacrylate were used as seeds in the dispersion polymerization of styrene in the presence of a polymeric stabilizer, poly(1,1-dihydroheptafluorobutyl methacrylate-*co*-diisopropylaminoethyl methacrylate) to produce dry composite particles. The transmission electron microscopy analysis revealed that the composite microspheres contained several silica particles.

Keywords Composite particles · Surface grafting · Silica · Polystyrene · Dispersion polymerization · Supercritical carbon dioxide

Introduction

Encapsulation technologies are becoming more and more popular, since polymer-encapsulated inorganic oxide particles can offer very interesting actual and potential applications such as in adhesives, optics, textiles, and electronics [1–3]. The incorporation of inorganic materials on the nanoscale can enhance fire retardancy [4] and mechanical strength [5, 6] of organic polymers and coatings. Owing to the many uses of silica, different methods for the synthesis of polymer/silica nanocomposite particles have been reported. Though a wide variety of methodologies were employed to synthesize polymer/silica composites, a traditional method of producing polymer-encapsulated silica nanocomposite particles has been emulsion polymerization. Dispersion polymerization was also reported to be a possible method of preparing polymer-encapsulated silica nanocomposite particles. Bourgeat-Lami and Lang [7, 8] reported the synthesis of polystyrene/SiO_2 composite particles by dispersion polymerization of styrene in polar media in the presence of surface-functionalized silica particles using 3-(trimethoxysilyl) propyl methacrylate (MPS) as the coupling agent. In a related work, Sondi et al. [9] described stable dispersions of nanosilica coated with *tert*-butyl acrylate polymer by in situ polymerization of monomer in 2-propanol. Various polymer/metal oxide nanocomposites including silica have been reported for different requirements [10–14]. However, processing of polymers generally employs a large quantity of organic solvents that are noxious and harmful to the environment. Thus, the processing with supercritical fluids attracts a great interest as an alternative to the conventional processing.

During the past decade, supercritical carbon dioxide ($scCO_2$) has attracted a great deal of attention as an "environmentally benign, inexpensive, and non-flammable alternative" solvent for polymer synthesis and processing [15]. The low viscosity, near-zero surface tension, relative chemical inertness, and high diffusivity of $scCO_2$ result in negligible competitive adsorption with guest molecules on

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the host substrate and therefore facilitate solute transfer relative to conventional solvents. Furthermore, since CO_2 is a gas at ambient conditions, the tedious drying procedure associated with conventional liquid solvents is circumvented, and the product is free of residual solvent upon depressurization. These unique properties of $scCO_2$ have been exploited to prepare polymer blends [16]. The usual method employs $scCO_2$ as a swelling agent to facilitate the diffusion of a guest monomer into a CO_2-swollen polymer matrix. Subsequent polymerization develops a blend of submicron phase-separated polymers. Several other research groups have attempted to prepare polymer/inorganic filler nanocomposites in $scCO_2$ [17–20]. Recently, Wang and co-workers reported the synthesis of polystyrene/C_{60} composite microparticles by one-step seed dispersion polymerization in $scCO_2$ although they could not observe C_{60} in the PS matrix [21]. More recently, PMMA/SiO_2 [22], PVAc/SiO_2 [23], and PPy/TiO_2 [24] nanocomposites were synthesized in $scCO_2$. Though few studies have been reported on polymer/inorganic oxide composite microspheres in $scCO_2$, particularly there has been no report in the literature so far based on the synthesis of composite microparticles where inorganic fillers were embedded inside the polymer matrix.

In this study, we introduced an effective method to synthesize polystyrene/silica (PS/SiO_2) composite microparticles through the dispersion polymerization of styrene with surface-modified SiO_2 in $scCO_2$. The resulting composite powder was characterized by various techniques including Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).

Experimental section

Materials

Styrene (Sigma-Aldrich), diisopropylaminoethyl methacrylate (DPAEMA; Sigma-Aldrich), and 1,1-dihydroheptafluorobutyl methacrylate (FBMA; Sigma-Aldrich) were purified by passing through a neutral alumina column to remove an inhibitor. Then, they were stored over CaH_2 below 0 °C and distilled prior to use. Silica nanoparticles whose average diameter was 130 nm were synthesized by the so-called Stober method [25]. 3-(Trimethoxysilyl) propyl methacrylate (Sigma-Aldrich), methanol (Sigma-Aldrich), and research-grade CO_2 (Daeyoung Co., 99.99%) were used as received. 2,2′-Azobisisobutyronitrile (AIBN; Sigma-Aldrich) was recrystallized in methanol before use. Toluene (Sigma-Aldrich) was distilled over CaH_2 prior to use.

Grafting of MPS onto silica nanoparticles

The grafting reaction was carried out according to the procedure given in the literature protocol [26]. After dispersing 2.5 g of silica nanoparticles in 50 mL of toluene, an excess amount of MPS was added and the resulting solution was stirred for 24 h under argon atmosphere. The MPS-modified silica was isolated by centrifugation and washed repeatedly with toluene. Finally, it was dried at 60 °C under vacuum for 24 h.

Preparation of polymeric stabilizer

The random copolymeric stabilizer composed of FBMA and DPAEMA (poly(FBMA-*co*-DPAEMA)) was prepared according to our previous procedure [27, 28]. In a typical polymerization, a 25-mL flask equipped with a stir bar was charged with 0.70 g of FBMA, 0.30 g of DPAEMA, and 0.01 g of AIBN. The flask was purged with argon and heated to 65 °C for 24 h. After polymerization, the reaction mixture was dissolved in the mixture of $CFCl_3$ and chloroform, and the solution was poured into hexane to precipitate the copolymer. The product was filtered and dried. The weight composition of monomers incorporated in the random copolymeric stabilizer was determined to be 69:31 for FBMA/DPAEMA by ^1H NMR analysis. The number average molecular weight of the copolymer was determined to be 49,500 by gel permeation chromatography using THF as an eluent.

Synthesis of PS/SiO_2 composite particles in $scCO_2$

The synthesis of composite particles by dispersion polymerization of styrene (St) in the presence of MPS-grafted silica in $scCO_2$ was carried out in a 4-mL high-pressure view cell reactor equipped with sapphire windows which permit visual observation of the reaction mixture. In a

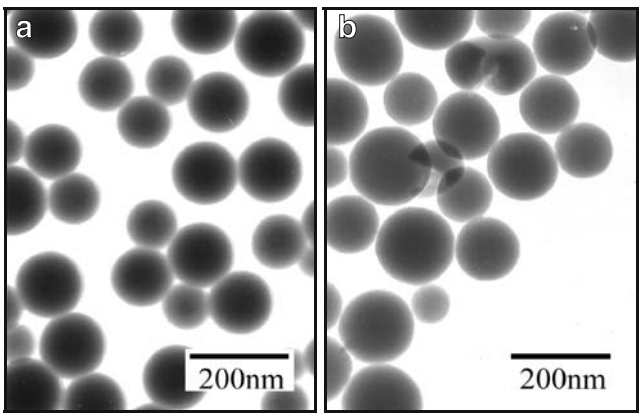

Fig. 1 TEM images of (**a**) as-prepared and (**b**) MPS-grafted silica particles

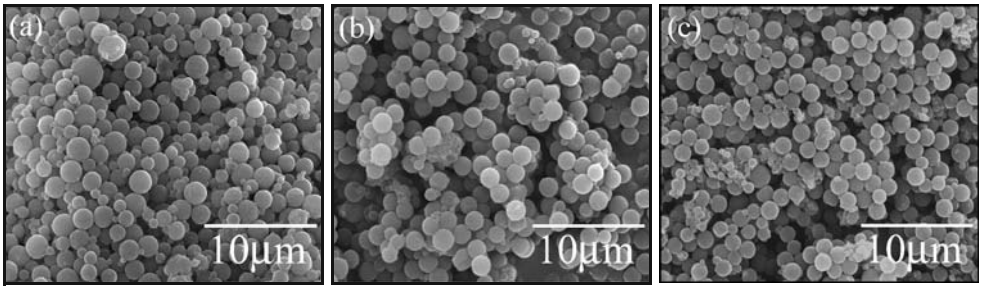

Fig. 2 SEM images of (**a**) neat PS and PS/SiO_2 composites, (**b**) C-1, and (**c**) C-2

typical polymerization, 0.6 g of styrene, 0.03 g of MPS-grafted silica, 0.06 g of stabilizer poly(FBMA-*co*-DPAEMA), 0.006 g of AIBN, and a Teflon-coated stir bar were placed in the stainless steel reactor. MPS-grafted silica was previously dispersed in styrene using a sonifier (Branson 450) before adding them into the reactor. An ISCO Model No. 260D automatic syringe pump was used to pressurize the reactor with CO_2 to approximately 70 bar, and the reaction mixture was heated to 65 °C. As the reaction vessel was heated, more CO_2 in the syringe pump was added into the system until the desired pressure (345 bar) was reached. The reactor was sealed and polymerization was carried out for 40 h. After polymerization, the reactor was cooled in an ice water bath, and the unreacted styrene was extracted with liquid CO_2 at a flow rate of 20 mL/min. The dry product was removed from the reactor and weighed.

Characterization

TEM images were obtained on a transmission electron microscope (JEOL, JEM-2010) operated with an accelerating voltage of 200 kV. A Hitachi S-2400 scanning electron microscope was used to measure particle size of the latex particles. Thermal stabilities of PS and PS/SiO_2 composites were investigated by a thermal gravimetric analyzer (Perkin Elmer, TGA-7) with a heating rate of 10 °C/min under nitrogen flow (35 mL/min). FT-IR characterizations of PS and the composites were performed using a BOMEM Hartman & Braun spectrometer.

Results and discussion

In order to produce PS/SiO_2 composite latexes in $scCO_2$ successfully, it is necessary to disperse silica nanoparticles in the mixture of styrene and $scCO_2$ prior to the polymerization. We prepared silica nanoparticles with average particle size of 130 nm, which have well-defined spherical shape and monodispersity as proven by TEM (see Fig. 1a). Then, the silica nanoparticles were surface-functionalized with MPS. The surface-modified silica was characterized by TEM (Fig. 1b) and FT-IR (Fig. 4d). The FT-IR spectrum showed characteristic absorption bands: CH_3 (2,952 and 1,450 cm^{-1}), C=O (1,717 cm^{-1}), C=C (1,632 cm^{-1}), and Si–O–Si (1,096 and 460 cm^{-1}) asymmetric and symmetric vibrations, which indicated the availability of silane group on the surface of SiO_2 particles [7]. The surface-modified silica showed better dispersion in the polymerization medium than pristine SiO_2 probably due to hydrophobicity on the surface. The MPS functionalization not only changed the silica surface into hydrophobic, but also it provided methacrylate terminal groups for polymer grafting. The surface grafting of MPS was expected to promote the anchoring of PS chains on the silica surface by copolymerization with styrene monomer during dispersion polymerization.

The MPS-grafted silica particles were used as seeds in the dispersion polymerization of styrene stabilized by the polymeric dispersant, poly(FBMA-*co*-DPAEMA) in $scCO_2$. It was proven that this method was useful to obtain well-defined composite microparticles. The resulting composite particles possessed good dispersibility in $scCO_2$ and were produced at high yield. Polymerization reactions were carried out with a fixed amount of monomer (15% *w*/*v* to CO_2) and stabilizer (10% *w*/*w* to monomer), but with varying amounts of silica nanoparticles (5% and 10% *w*/*w* to monomer). As a comparison, neat polystyrene microparticles were also prepared under precisely the same condition but in the absence of silica. At the initial stage of polymerization, the silica seed particles were well dispersed with stirring as viewed through a sapphire window. After 30 min of polymerization, the solution became white and it was hard to identify the spin bar inside

Table 1 Characterization of silica–PS composites prepared with copolymeric stabilizer, poly(DPAEMA-*co*-FBMA) (31:69)

Sample	MPS-grafted SiO_2 (% *w*/*w* to St)	D_n[a] (μm)	Yield (%)
PS	0	1.41	92
C-1	5	1.45	92
C-2	10	1.60	90

Reaction conditions: 15% St (*w*/*v* to CO_2), 1% AIBN (*w*/*w* to St), 10% stabilizer (*w*/*w* to St), at 65 °C, with the initial pressure of 345 bar for 40 h

[a] Particle diameter was determined from TEM.

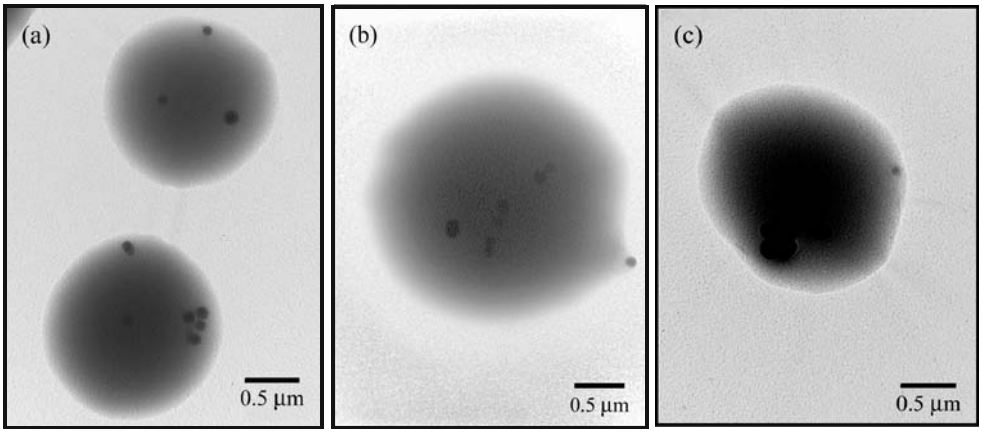

Fig. 3 TEM images of (**a**) PS/SiO_2 composites, (**b**) C-1, and (**c**) C-2

the reactor. The product collected after 40 h was agglomerated but was easily broken up into a powder with a spatula as it was removed from the reactor. The results are summarized in Table 1 and Fig. 2. Figure 2 shows the representative scanning electron micrographs of PS and PS/SiO_2 composites from the dispersion polymerization. The PS obtained from the polymerization was in the form of spherical particles with an average particle size of 1.41 μm and showed relatively broad particle size distribution. SEM images of PS/SiO_2 composites showed also spherical micron-sized particles, but a few aggregates of smaller particles could be seen together in the micrographs (especially in Fig. 2c). This can be attributed to the pre-aggregation of bare silica particles mainly taking place during the ultracentrifugation/redispersion procedure to purify the MPS-grafted silica. The silica aggregates might not be separated completely into individual particles in the reaction solution prior to polymerization, which is likely the reason for the heterogeneity of morphologies including encapsulated particles, small aggregates, and free PS particles.

Figure 3 shows TEM images of PS/SiO_2 composite microspheres, where dark silica nanoparticles of 130 nm are embedded inside light PS shells. Free polystyrene particles that did not contain a silica particle were also present (figure is not shown). It was considered that primary particles were incorporated in the composite latex in individual or slightly agglomerated form via either absorption or copolymerization with styrene, which was stabilized by the copolymeric dispersant, poly(FBMA-*co*-DPAEMA). The multi-core microsphere might originate from the association, during the polymerization, of several latex particles, each of them containing one silica bead or small

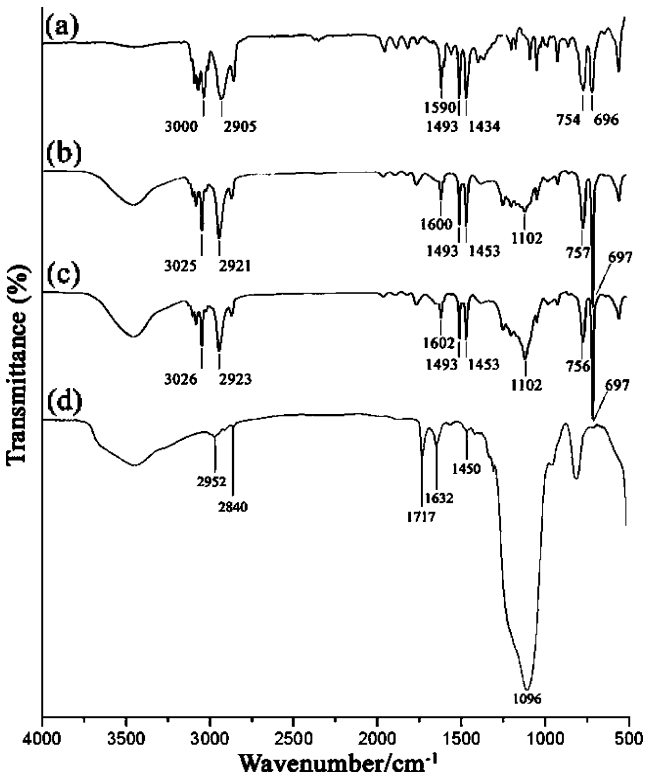

Fig. 4 FT-IR spectra of (**a**) PS, (**b**) C-1, (**c**) C-2, and (**d**) MPS-grafted silica particles

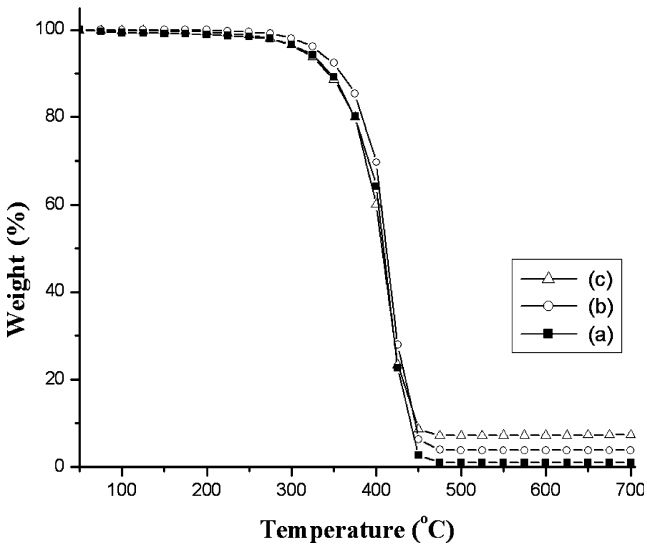

Fig. 5 TGA plots of (**a**) PS, (**b**) C-1, and (**c**) C-2

aggregate. The composite particle morphology, as illustrated in Fig. 3b, especially tends to confirm this hypothesis. It is known that the polystyrene chains grow in the continuous phase and reach a particular molecular weight at which they are no longer soluble. At this point, either the polymer chains precipitate on the silica surface by partially copolymerizing with the methacryloyl groups on the surface, or they associate with other growing polymer chains in the continuous phase and form small polymer aggregates. Associations between composite particles could happen until the concentration of stabilizer at the surface of the polymer is high enough to ensure a good stabilization of the particles which then contain several silica beads. Supercritical CO_2 offers high monomer diffusivity for the growth of the tethered chains. It also brings the plasticization effect that increases the chain mobility and enhances the incorporation of SiO_2 particles into the polymer matrix. A similar trend was previously observed in an aqueous ethanol medium by others, where the encapsulation of silica beads was achieved by the dispersion polymerization of styrene in the presence of MPS-modified silica using poly(*N*-vinyl pyrrolidone) stabilizer [7]. Each composite particle contained several silica beads, the number of which depended on the size of silica particles and on the silica content. It was explained that the association might occur in the course of the polymerization due to the close mean distance between the surfaces of two adjacent silica beads in the reaction medium and a lack of stabilizer, especially with smaller silica beads [8].

Information on the structure of PS/SiO_2 composites was also obtained from FT-IR analysis along with PS standard and MPS-modified silica. Figure 4 a shows the spectrum of PS with the usual characteristic bands at 1,434, 1,493, and 1,590 cm^{-1} (aromatic C–C stretching), 696 and 754 cm^{-1} (aromatic C–H bending), and 2,900–3,100 cm^{-1} (aromatic C–H stretching). As expected, the spectra of the composite (see Fig. 4 b and c) clearly exhibited absorption bands attributed to both PS (3,026, 1,602, 1,493, 1,453, 756, and 697 cm^{-1}) and silica (1,102 cm^{-1}). The absorption band at 1,102 cm^{-1} (Si–O–Si) which increases with silica feed ratio indicates that the silica nanoparticles have been incorporated in the composite. Comparing the infrared spectrum of the composite particles with MPS-modified silica, it is obvious that the C=C (1,632 cm^{-1}) band disappeared after the polymerization. The results indicate that MPS bonded to the silica surface, and styrene monomer copolymerized on the surface of grafted silica particles to produce the encapsulated morphology.

Figure 5 shows the thermogravimetric analysis plots of PS and PS/SiO_2 composites. The weight loss between 350 and 450 °C in the composite particle, which is consistent with the degradation of pure PS, is attributed to the existence of PS. The residual amounts of PS and composites C-1 (5% silica) and C-2 (10% silica) were determined to be 0.7%, 3.8%, and 7.3%, respectively. TGA results also suggest that PS/SiO_2 composites have higher thermal stability than neat PS.

Conclusion

A facile approach to synthesize PS/SiO_2 composite microparticles in $scCO_2$ has been developed in this study. The surface modification of silica particles with MPS provided both the good dispersion of the particles in the polymerization mixture of styrene and CO_2 and the anchoring of PS on the silica. The random copolymer, poly(FBMA-*co*-DPAEMA) served as an effective stabilizer for the polymerization of styrene in $scCO_2$ without agglomeration of composite latexes. It is proposed that the stabilizer provides steric stabilization on the composite particles in CO_2 continuous phase, and the surface-grafted silica particles bearing methacrylate terminal groups promote the polymer absorption. The resulting powder consisted of composite microparticles and free PS particles. The TEM analysis of the composite microparticles showed that several silica nanoparticles were embedded inside the PS microsphere. FT-IR and TGA data also confirmed the composite formation. This radical dispersion polymerization route allows for the clean and dry synthesis of inorganic oxide/polymer composite microparticles with high yields.

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