

PREPARATION OF INORGANIC / POLYMER NANOCOMPOSITE PARTICLES BY DISPERSION POLYMERIZATION IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

In this study, we demonstrated that SiO₂/polymer nanocomposite particles were produced by dispersion polymerizations in scCO₂. Nano-sized silica particles surface modified with 3-(trimethoxysilyl) propyl methacrylate were used as seeds in the dispersion polymerization of styrene or MMA in the presence of polymeric stabilizers to produce dry composite powder. It was found that the products had relatively broad particle size distributions and inhomogeneous morphologies from the scanning electron microscopy and transmission electron microscopy (TEM) analyses. TEM also revealed that most composite particles contained several silica particles in the polymer matrix.

INTRODUCTION

Inorganic/polymer composites are attractive materials by the insertion of inorganic particles into polymeric matrices. They are expected to combine the unique properties of the inorganic particles and organic polymers. Especially the preparation of core-shell composite particles has received particular attention due to their great potential applications such as adhesive, 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 and emulsion polymerization was a traditional method of producing synthesizes polymer/silica composites. Dispersion polymerization was also reported to be a possible method of preparing polymer encapsulated silica nanocomposite particles. Accordingly, a number of researches have been demonstrated to make use of dispersion polymerization of polystyrene/SiO₂ composite in polar media as solvent.[7-14] However, processing of polymers generally employs 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 (scCO₂) has attracted a great deal of attention as a cheap, non-toxic, non-flammable, zero surface tension, high diffusivity and environmentally benign solvent for polymer synthesis and processing. These unique properties of scCO₂ have been exploited to prepare polymer blends [15]. Since carbon dioxide is recognized as a good solvent for most liquid vinyl monomers and a poor solvent for most polymers, it has been used as a medium for dispersion polymerization. It has unique characteristics such as high mass transfer rate and tuneable solvent power. It also has advantage of easy separation from products so that it can resolve problems related to solvent removal. Supercritical carbon dioxide dissolves low molecular weight organic compounds and swells most organic polymers, and thus it has been successfully utilized in the synthesis of polymer/polymer composites. Recently, Wang and co-workers reported the synthesis of polystyrene/C60 composite microparticles by one-step seed dispersion polymerization in scCO₂ although they could not observe C60 in the PS matrix [16]. More recently, PMMA/SiO₂ [17], PVAc/SiO₂ [18] and PPy/TiO₂ [19] nanocomposites were synthesized in scCO₂. Though few studies have been reported on polymer/inorganic oxide composite microspheres in scCO₂, particularly there has been no report in the literature so far based on the synthesis of core-shell type particles where inorganic fillers were embedded inside the polymer matrix.

In this study, we introduced an effective method to synthesize PMMA/SiO₂ core-shell sub-microparticles through the dispersion polymerization of methyl methacrylate(MMA) with surface modified SiO₂ in scCO₂.

EXPERIMENTAL

Silica nanoparticles of average diameter 121 nm were synthesized by Stöber method [20]. The grafting reaction on the silica particles was carried out with 3-(trimethoxysilyl) propyl methacrylate (MPS). In the procedure, 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. The product was dried at 60 °C under vacuum for 24 h. The copolymeric stabilizers, random copolymers of 1,1-dihydroheptafluorobutyl methacrylate (FBMA) and oligoethylene glycol methacrylate (OEGMA) or diisopropylaminoethyl methacrylate (DPAEMA) were prepared by free radical polymerization. For poly(FBMA-*co*-OEGMA), a 25 mL round bottom flask equipped with a stir bar was filled with 1.6 g of FBMA, 0.4 g of OEGMA, 0.02 g of AIBN and 2 ml of toluene as a solvent. The polymerization was performed at 70 °C for 12 h under nitrogen atmosphere. After polymerization, the reaction mixture was poured into hexane to precipitate the polymer. The copolymer product was filtered and dried under vacuum. The molar composition of FBMA and OEGMA was determined to be 94 mol % and 6 mol % by ¹H NMR analysis. Poly(FBMA-*co*-PPAEMA) (64 : 36) was prepared in the same manner. The molecular structures of the copolymeric stabilizers are depicted in Fig. 1.

The synthesis of composite particles by dispersion polymerization in scCO₂ was carried out in a 4 mL high-pressure view cell reactor. In a typical polymerization, 0.9 g of MMA, 0.1 g of MPS-grafted silica, 0.1 g of poly(FBMA-*co*-OEGMA), 0.009 g of AIBN, and a Teflon-coated stir bar were placed in the reactor. MPS-grafted silica was previously dispersed in MMA 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 CO₂ to approximately 70 bar, and the reaction mixture was heated to 65 °C. As the reaction vessel was heated more CO₂ 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 12 h. After polymerization, the reactor was cooled in an ice water bath, and unreacted MMA was extracted with liquid CO₂ at the flow rate of 20 mL/min. The dry product was removed from the reactor and weighed.

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 (SEM) was used to measure the particle size of the composite particles.

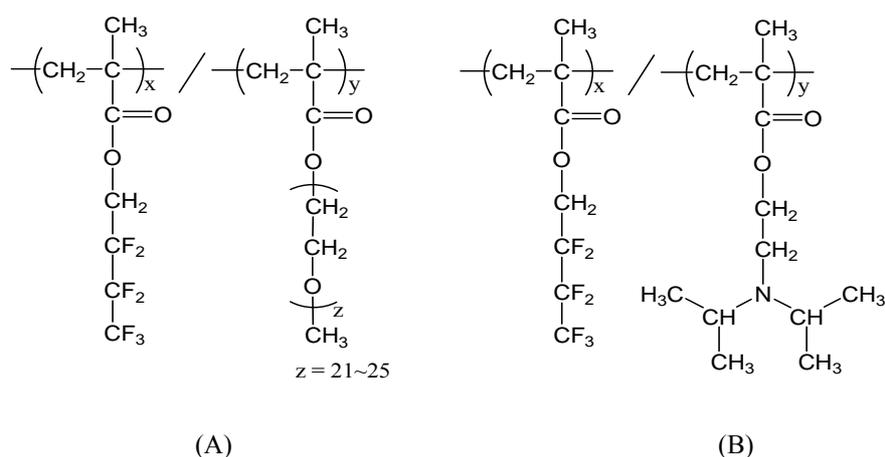


Fig. 1. The molecular structure of (A)poly(FBMA-*co*-OEGMA) and (B)poly(FBMA-*co*-DPAEMA)

RESULTS AND DISCUSSION

In order to produce SiO₂/polymer composite latexes in scCO₂ successfully, it is necessary to disperse silica nanoparticles in the mixture of monomer and scCO₂ prior to the polymerization. Silica nanoparticles of average particle size 121 nm were prepared and then they were surface functionalized with MPS [19]. The surface modified silica showed better dispersion in the polymerization medium than pristine SiO₂. MPS was expected to promote the anchoring of polymer chains on the silica surface by copolymerization with monomers during the dispersion polymerization. The proposed schematic representation for the synthesis of composites is illustrated in Fig 2.

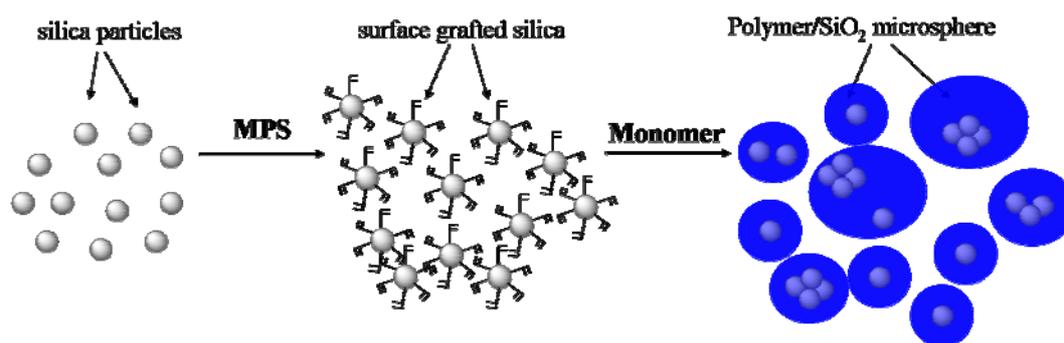


Fig. 2 Schematic representation of the process for the synthesis of SiO₂/polymer composite particles in scCO₂

Table 1. Characterization of silica/polymer composites prepared with copolymeric stabilizer. Reaction condition: 1 % AIBN (w/w to monomer), 10 % stabilizer (w/w to monomer), temp 65°C, initial pressure 345 bar

Sample ^a	Monomer	Surfactant	MPS-grafted SiO ₂ (w/w% to Monomer)	D _n ^b (μm)	PSD ^b	Yield (%)
1	MMA	poly(FBMA- <i>co</i> -OEGMA)	10	1.71	1.14	92
2	Styrene	poly(FBMA- <i>co</i> -DPAEMA)	10	1.26	1.04	90

^a polymerization time : 12 h for Sample 1 and 40 h for Sample 2, monomer concentration : 23 w/v % for Sample 1 and 15 w/v % for Sample 2.

^b particle diameter was determined from SEM.

The MPS-grafted silica particles were used as seeds in the dispersion polymerization of MMA or styrene stabilized by the polymeric dispersants in scCO₂. It was proven that this method was useful to obtain composite latexes in CO₂. The resulting composite particles possessed good dispersibility in scCO₂ and were produced at high yield. At the initial stage of polymerization, the silica seed particles were well dispersed with stirring as viewed through the sapphire window. After 30 min of polymerization, the solution became milky and it was hard to identify the spin bar inside the reactor. The product collected after the polymerization was easily broken up into a powder with a spatula as it was removed from the reactor. Fig. 3(A) and (B) shows scanning electron micrographs of PMMA/SiO₂ and PS/SiO₂ composites from the dispersion polymerizations, respectively. The SiO₂/polymer obtained from the polymerization was in the form of spherical particles with the average particle size of 1.71 μm for PMMA and 1.26 μm for PS. The powder had broad particle size distribution indicating the effective but insufficient stabilization of the copolymeric dispersants on the

polymerization. Poly(FBMA-*co*-OEGMA)/MMA system resulted in the composites of bigger particles with broader particle size distribution than poly(FBMA-*co*-DPAEMA)/styrene system. Fig. 4(A, B) and (C, D) shows TEM images of PMMA/SiO₂ and PS/SiO₂ composites, where dark silica nanoparticles are embedded inside light polymer shells. Most of the composite particles contained more than one silica bead. Free polymer particles that did not have a silica particle were also present (figure is not shown). The pre-aggregation of MPS-modified silica particles is likely the main reason for the irregular morphologies. It is considered that the MPS-modified silica is not separated completely into individual particles in the reaction solution prior to the polymerization. Primary particles are incorporated in the composite latex as individual or slightly agglomerated form via either absorption or copolymerization with monomers, which is stabilized by the copolymeric dispersants. The other possibility is 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 stabilizers for the small silica beads.[8] It is known that polymer 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 silica beads.

Supercritical CO₂ 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 SiO₂ particles into the polymer matrix.

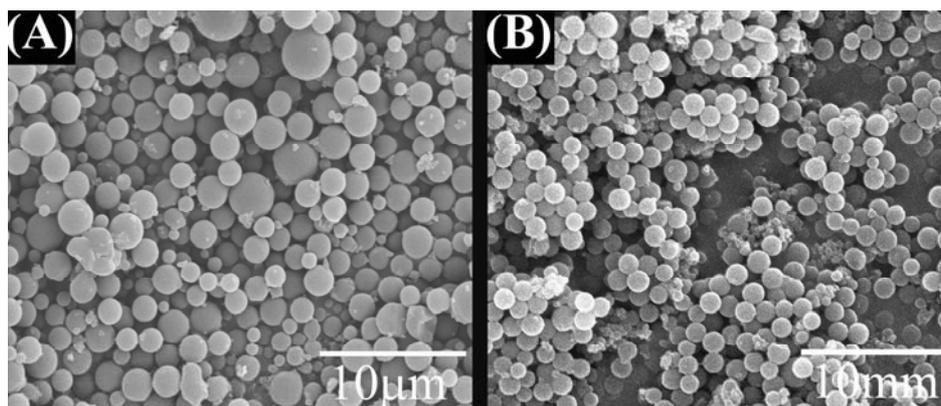


Fig. 3 SEM images of (a) PMMA/SiO₂ and (b) PS/SiO₂ nanocomposite particles.

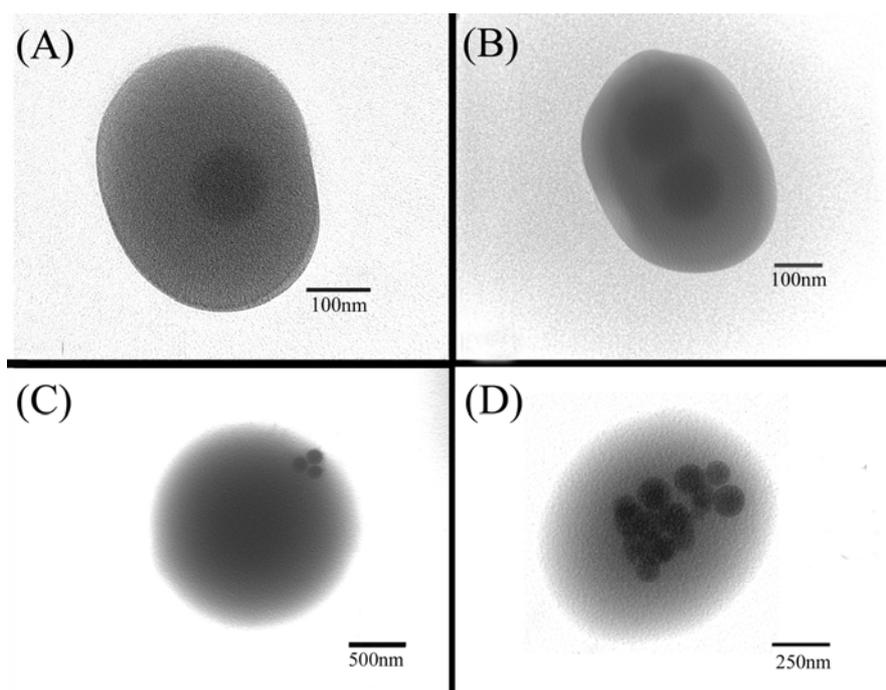


Fig. 4 TEM images of (A , B) PMMA/SiO₂ and (C, D) PS/SiO₂ nanocomposite particles.

CONCLUSIONS

An approach to synthesize SiO₂/polymer composite particles in scCO₂ 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 monomer and CO₂ and the anchoring of polymer on the silica. It is proposed that the copolymeric stabilizers provide steric stabilization on the composite particles in CO₂ continuous phase and the methacryloyl terminal group of MPS improves the polymer absorption on the seed particles. The morphologies were heterogeneous due to the pre-aggregation of seed particles. TEM analysis of the composite particles showed that most polymers encapsulated several individual or agglomerated SiO₂ particles.

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