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Title:
Sparsely Distributed Silica/PMMA Composite Particles Prepared by Static Polymerization in Aqueous Silica Dispersion

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Abstract:
Silica/poly(methyl methacrylate) (PMMA) composite particles, in which silica particles are sparsely distributed in the surface of PMMA particles, were formed by static dispersion polymerization of methyl methacrylate (MMA) in aqueous dispersions of submicron silica particles. The silica-modified PMMA particles were constructed via Pickering emulsion-like silica/PMMA aggregation based on weak interaction between PMMA and silica. The morphology of the composite particles is governed by the adsorption/partition equilibrium of PMMA with the silica surface.

Keywords:
Organic-inorganic composite materials, Static dispersion polymerization, Silica particles, Poly(methyl methacrylate)

Main Text

1. Introduction

The field of organic-inorganic nanocomposite particles has become the subject of rapidly growing interest [1-11]. Such materials are expected to provide a new class of building blocks and exhibit unusual, possibly unique optical, mechanical, rheological, electrical, catalytic and flame retardant properties [12-19]. Of the various nanostructures of organic-inorganic composite particles, core-shell nanocomposite particles in which polymer particles (core) are coated by smaller silica particles (shell) have been extensively reported [2, 20-28]. Polymer particles coated by smaller
inorganic nanoparticles have been prepared by dispersion [21-23] and soap-free aqueous emulsion 
[17, 24, 27] polymerization with dispersed nano-scale silica sols.

Raspberry-like silica/poly(methyl methacrylate) (PMMA) composites have been prepared by 
copolymerization of Pickering emulsions [29, 30] with methyl methacrylate (MMA) and 
vinylimidazole in an aqueous silica dispersion [20]. The Pickering emulsion is formed by strong 
acid-base interaction between hydroxyl groups on the silica surface and amino groups on 
vinylimidazole. Armes et al. have described another synthesis methodology for preparing core-shell 
nanocomposites by dispersion polymerization of styrene, MMA and methacrylate analogues initiated 
by anionic [21] or cationic [22] initiator, in aqueous alcoholic media with silica nanoparticles. In 
certain conditions, the polymer aggregates formed in the dispersion during polymerization are 
stabilized by the electrostatic repulsion of silica adsorbed on the surface. Aqueous emulsion 
polymerization of MMA with glycerol-modified nanosilica has been also reported to produce 
core-shell nanocomposite particles [17]. Introduction of the glycerol moiety might decrease the 
negative surface charge and increase the affinity with monomer to help form nanoparticle-armored 
polymer composite structures with higher nanoparticle content.

In this article we report polymer/inorganic composites, in which submicron-scale silica particles 
are sparsely distributed on the surface of PMMA particles, made by surfactant-free static 
polymerization of MMA in an aqueous silica dispersion. Polystyrene particles sparsely coated with 
20 nm silica particles, and with silica content as low as ~1%, were prepared by dispersion 
polymerization of styrene in an alcoholic silica sol by Schmid et al [23]. In the present study, it was 
found that composite particles with such sparsely silica coated structure can be produced from a very 
simple polymerization system, in which static thermal dispersion polymerization of MMA, initiated 
by a lipophilic initiator, is conducted in aqueous silica dispersion without surfactant and without 
agitation. The key factor in forming the sparsely-coated silica-PMMA structure is the weak 
interaction between PMMA and silica particles.

2. Materials and Methods

2.1. Materials

Methyl methacrylate (MMA), styrene, ethyl methacrylate and butyl methacrylate were 
purchased from Wako Co., Japan and passed through a disposable column (Sigma-Aldrich, USA) to 
remove inhibitors. The radical initiator 2,2'-azobisisobutyronitrile (AIBN; Wako Co., Japan) was 
used without further purification. Commercially available silica particles (MP-2040, Nissan 
Chemical Co.; average diameter 200 nm) and silica nanoparticles (OSCAL1132, Syokubai Chemical 
Co.; 20 nm diameter) were purified by at least four centrifugation/re-dispersion cycles (High-Speed 
Refrigerated centrifuge; Hitachi CR20G) with pure water. Surface charge potentials (ζ potentials) of
the silica particles (200 nm) were affected by acidity (-17 mV at pH 3.1) and basicity (-36 mV at pH 10.1) of the aqueous medium. Water (R > 15 MΩ) purified using a Milli-Q system (Millipore Co. Ltd.) was used to prepare aqueous solutions.

2.2. Synthesis

A typical static polymerization procedure for MMA in silica particle dispersion was as follows. An aqueous dispersion of silica particles (diameter ca. 200 nm; 3 wt% relative to water) was saturated with MMA together with AIBN (1 wt% relative to MMA) by manual shaking for 1 minute. To remove oxygen the dispersion was degassed by three cycles of cooling and nitrogen flushing before sealing the reactor. After standing for 1 h at room temperature, the MMA-silica particle dispersion was heated at 60°C for 24 h without agitation (i.e. in static polymerization conditions). Purification was conducted by washing with pure water and three cycles of centrifugation/re-dispersion (5000 rpm; 25 min). Excess silica particles were entirely removed from each supernatant solution.

2.3. Characterization.

Average particle diameter in pure water was determined by particle size distribution analysis using dynamic light scattering (DLS; EL-4000k, Otsuka Electronics Co. Ltd.). The morphology of the synthesized particles was observed using scanning electron microscopy (SEM; Tiny SEM, Technex Lab. Co. Ltd.) with 5.0 kV accelerating voltage, and transmission electron microscopy (TEM; JEOL JEM-2000X) at 80 kV accelerating voltage. The SEM and TEM samples were prepared by placing drops of aqueous dispersions of the particles onto mica sheets and carbon mesh Cu grids supported with formvar film, respectively. For SEM, the samples were sputter-coated with gold prior to observation. To determine the silica and PMMA contents, thermogravimetric analysis (TGA; TG/DTA6300, SEIKO Instruments Japan) was carried out on vacuum-dried samples in air at a heating rate of 10°C min⁻¹ at temperatures up to 800°C. The mass loss in the temperature range 350-400°C was attributed to quantitative pyrolysis of the organic component, and the incombustible residue was assumed to be silica.

3. Results and Discussion

Fig. 1a shows the stable, dense milky-white dispersions that were predominantly obtained from the static polymerization reaction. A small amount of sedimentation was observed after polymerization, and excess monomer separated as an upper phase on the aqueous phase and formed a PMMA bulk polymer. Fig. 1b shows a typical SEM image of the product prepared by simple
casting immediately after polymerization. The product consisted of bare silica and rugged silica-modified PMMA particles.

The amount of MMA consumed by polymerization was estimated to be typically 6.9 wt% of the dispersion, by subtracting the separated bulk PMMA in the upper phase. Since the solubility of MMA in pure water is 1.6 wt%, the MMA consumed in the polymerization in the silica dispersion was replenished by diffusion of MMA from the excess in the upper phase.

Silica-modified PMMA particles were easily separated from the mixed dispersion by gentle centrifugation (5000 rpm, 25 min); free silica that was not attached to PMMA particles could be sedimented at 20000 rpm. The apparent ratio of free silica to silica-modified polymer product, estimated by TGA before and after purification, indicated that 58 wt% of the available silica was incorporated into the polymer product. The silica-modified particles were able to be re-dispersed in pure water. After purification of the particles by at least three cycles of centrifugation and re-dispersion, milky-white dispersions consisting only of silica-modified PMMA particles were obtained. The yield of polymer product after purification was calculated to be 85% from the polymer weight obtained by TGA.

Characterization data for selected polymerization conditions are summarized in Table 1. SEM and TEM images (Figs. 2a and b) of the purified silica-modified particles indicate that the sample consisted almost entirely of relatively monodisperse silica-modified PMMA particles (Run 1 in Table 1). In the composite particles, interestingly, silica particles with diameter 200 nm did not fully cover but were randomly and sparsely distributed on the surface of the PMMA particles. The TEM image shows that the silica particles were immobilized by partial burial in the PMMA particle surfaces. The silica particles were located only at the surface of PMMA particles and not within the polymer cores.

Typical average sizes of the composite particles and the PMMA particles without silica were evaluated as 710 nm (polydispersity index 1.19) and 685 nm (polydispersity index 1.14), respectively, by dynamic light scattering (DLS). The diameters from DLS and electron microscopy images were in accordance. It should be noted that the polymerization gave highly reproducible particle shape and size. The average number of silica particles on a PMMA particle, calculated from the volume ratio estimated from the average diameter (DLS), and the volume fraction assumed from the weight ratio determined by TGA, was approximately 11. From the electron microscopy images it appeared that each composite particle carried ca. 10 silica particles on the surface (Fig. 2b and the inset). The average number of silica particles found from expanded scale TEM images thus agreed with that from TGA. The silica particles remained on the polymer particle surface even after purification that included sonication and centrifugation, indicating the stability of the composite particles.

To remove the embedded silica particles, the composite particles were immersed in concentrated KOH solution for 1 week, then washed many times with water. After the alkali treatment, the PMMA
particles exhibited a pock-marked surface with cavities (Fig. 2c) where silica had been located. This experiment showed that the silica particles had been embedded in the surface of the PMMA particles with significant penetration depth. Despite the relatively large (almost μm) size of the particles, the dispersion of silica/PMMA composite particles was stable for about 0.5 day and precipitation was observed over a period of 1 day. In addition, the particles could be re-dispersed by simple mixing by hand. The driving force of the colloidal dispersion is dominantly the ionic charges of the silica particles immobilized on the surface of PMMA.

The sparsely distributed silica-modified PMMA particles were constructed via Pickering emulsion-like silica/PMMA aggregation based on weak interaction between PMMA and silica. Fig. 3 presents a proposed mechanism for formation of the silica-modified polymer particles. Before polymerization, MMA monomer and AIBN were dispersed homogeneously in the aqueous silica dispersion. Because of the lack of hydrophilic initiator residues, oligomeric PMMA formed in the early stages of polymerization adsorbs onto silica by partition. Then the silica particles with adsorbed PMMA assemble to form a Pickering emulsion-like aggregate, in which relatively hydrophobic PMMA and hydrophilic silica provide a core and an outer shell, respectively. During polymerization, MMA monomer is continuously supplied from the aqueous solution to the inner PMMA core and the size of the PMMA cores increases, with the result that sparsely distributed silica-modified PMMA is formed. The number of silica particles attached to a PMMA particle should be determined at the stage of initial Pickering-like aggregation. In addition, the silica on the surface of the composite particles prevents secondary aggregation by electrostatic repulsion of the silica.

The static condition was essential to form the composite particle structure. Sparsely silica coated PMMA particles were not formed when dispersion polymerization was conducted with gentle stirring. Under those conditions intact PMMA particles were formed with a small quantity of polymer aggregation products. This result clearly proved the existence of the weak but key silica-PMMA interaction, which is easily disrupted by stirring. In the proposed formation mechanism in Fig. 3, the highlighted step “PMMA-adsorbed silica” in the very early stages would be the critical step because the silica-PMMA interaction would be easily disrupted by even gentle stirring.

The morphology of the composite-forming PMMA should be governed by the adsorption/partition equilibrium of PMMA with the silica surface. Hence the influence of polymerization conditions, specifically size of the silica particles (Runs 2 and 3 in Table 1), pH (Runs 4 and 5) and concentration of silica (Runs 6 and 7) was investigated. A similar polymerization process with larger silica particles (average diameter 450 nm) gave an unstable colloidal dispersion of both silica particles and PMMA particles, but not composite particles (Run 2). Flocculation of the polymer particles and sedimentation of the silica particles were simultaneously observed 2 h after the start of polymerization.
When smaller (20 nm) silica nanoparticles were used (Run 3), composite silica/PMMA particles 263 nm in size were formed (Figs. 4a and b). Flocculation or sedimentation were not observed in the colloidal solution. After purification by centrifugation, non-incorporated silica was entirely removed from the aqueous dispersion. A TEM image (Fig. 4c; magnifying Fig. 4b) showed that silica nanoparticles were incorporated into/onto PMMA particles. The fuzzy circles (ca. 200 nm) and smaller dark spots in the image are attributed to PMMA particles and silica nanoparticles, respectively. The silica content of the PMMA particles was 6 wt% by TGA, which was smaller than that in the composite particles formed by silica particles with 200 nm diameter. The average number of silica particles in a PMMA particle was counted from the images as several tens, which is roughly consistent with the value calculated from the weight fraction (typically 35 for Run 3 in Table 1). With decrease of the silica particle size, the hydrophobic partition of PMMA on silica is decreased because of the higher dispersion stability of silica in water, resulting in formation of few Pickering type aggregates. Consequently, the size of the PMMA cores was reduced.

The influence of the pH of the polymerization medium was investigated to elucidate the influence of the surface charge densities on the composite particle structure. The polymerization reactions were carried out in the presence of 200 nm silica particles and essentially the same conditions. Polymerization at an acidic pH<pKa of silica (approximately 3 to 4), gave a coagulated dispersion (Run 4 in Table 1), and the centrifugation/redispersion purification cycles gave a milky silica/polymer dispersion. The SEM image shows that the dispersion consisted of simple spherical particles with size ca. 200 nm (Fig. 5a), which matched the size of the silica particles used. No sparsely-coated silica/PMMA composite particles were found, but fusion of several particles was frequently observed. Interestingly, the particles were not only silica, but also newly and independently formed PMMA particles. In the TEM image (inset to Fig. 5a), the clearly distinguished darker and lighter circles are attributed to silica and PMMA particles, respectively. On the other hand, in the pH region 6-10 (Fig. 5b) sparsely distributed silica/PMMA composite particles similar to those prepared by polymerization at pH 7 were formed (Run 5 in Table 1). No significant changes in terms of the size of the PMMA core and the quantity of adsorbed silica were observed.

A weak interaction between the anionic charge of silica and PMMA is crucial for the formation of sparsely-coated composite particles. This supposition is supported by the observation that silica/PMMA composite formation did not occur at a pH lower than pKa of silica. In addition, the dependence on the chemical structure of the monomer was investigated. AIBN initiated static dispersion polymerization of the monomers styrene, ethyl methacrylate and butyl methacrylate gave a mixed dispersion of intact silica and polymer particles but not of silica/polymer composite particles. These results obviously proved that the interaction between silica and PMMA rather than AIBN residue plays an important role in forming such composite particles. Armes et al. have reported core-shell type PMMA particles coated with densely packed silica particles, prepared by dispersion polymerization with a cationic initiator [21, 22]. That behavior would be due to the
electrostatic interaction between silica and positive initiator residues on the polymers. The weak interaction to form sparsely-distributed silica/PMMA particles is thought to originate from the interaction between anionic charged silica and PMMA, and not between silica and AIBN residue.

The composite morphology was also sensitive to silica concentration. When polymerization was conducted in silica dispersions with lower silica concentrations (1.0 and 0.3 wt%), the dispersion showed obvious flocculation, indicating decreased dispersion stability due to lack of silica. Figs. 6a, b and c show the silica/PMMA composites prepared with silica concentrations 3.0, 1.0 and 0.3 wt% (relative to water), respectively. SEM observation was conducted using the purified products, which could be dispersed in water.

When the silica concentration was decreased from 3.0 to 1.0 wt%, sparsely-distributed silica/PMMA composites were still observed, and the size of the PMMA cores (ca. 500 nm) and number (roughly four or five) of attached silica particles were reduced (Fig. 6b; Run 6 in Table 1). At 0.3 wt% silica concentration the sparsely-coated structure was not observed and fused products consisting of a few PMMA or silica particles were formed. Dumbbell-like fused particles were regularly observed in a flocculated solution (Fig. 6c, and Run 7 in Table 1). The average size of PMMA particles (ca. 300 nm) decreased until they were slightly larger than the silica particles, and discrimination between silica and PMMA particles was difficult in the SEM image. Most particles were fused to each other, leading to flocculation.

Flocculation indicates reduced dispersion stability in the system and insufficient silica to stabilize the dispersion. The fact that the size of PMMA cores decreased with decreasing silica concentration indicates that the PMMA cores grew after the formation stage of Pickering-like aggregates. In conditions of insufficient concentration of silica (0.3 wt%), small PMMA particles, not supported by incorporated silica, might be formed before the fusion of particles including silica due to low dispersion stability. In other words, Pickering type PMMA particles prevent secondary aggregation. All results indicate that the unique composite structure was induced by weak attractive interaction between silica and PMMA and/or the partition equilibrium of PMMA between the aqueous phase and the silica surface.

4. Conclusions

Silica/PMMA composite particles with sparsely-coated structure were formed by static polymerization of MMA in aqueous dispersions of submicron silica particles. The fact that silica particles were embedded in the surface of the PMMA particles surfaces and not encapsulated indicates that the driving force for formation of this unique structure is a weak attractive interaction between silica and PMMA, and the thermodynamic partition of silica between the aqueous phase and MMA/PMMA phase. Controlling the balance of thermodynamic interactions in solution will be the key to constructing sophisticated nanostructures. In sparsely-coated particles, the unique
composite structure in which hydrophilic and hydrophobic moieties coexist on the particle surfaces will provide potential applications, such as chromatographic analysis, separation and bio-compatible materials.

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References


Fig. 1. Photograph of colloidal dispersion (a), and SEM image (b), of silica-modified PMMA particles including free silica particles, prepared by dispersion polymerization of MMA in aqueous dispersions of 200 nm silica particles, immediately after polymerization.

Table 1. Summary of the variation in silica content and particle diameter of the silica/PMMA composite and PMMA core particles with silica particle diameter, initial silica concentration and pH.

<table>
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<tr>
<th>Run</th>
<th>Silica diameter [nm]</th>
<th>Initial silica concentration [a] [wt%]</th>
<th>Solution pH</th>
<th>Silica content [b] [wt%]</th>
<th>Average diameter of composites [c] [nm]</th>
<th>Average diameter of core PMMA [d] [nm]</th>
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<tr>
<td>1</td>
<td>200</td>
<td>3.0</td>
<td>---</td>
<td>38.9</td>
<td>710±240</td>
<td>685±91 [f]</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>3.0</td>
<td>---</td>
<td>---</td>
<td>No particle formation</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1.0</td>
<td>---</td>
<td>6.1</td>
<td>263±64</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>3.0</td>
<td>pH 3.1</td>
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<td>172±14</td>
</tr>
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<td>pH 10.1</td>
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<td>711±69</td>
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<tr>
<td>6</td>
<td>200</td>
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<td>558±40</td>
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<tr>
<td>7</td>
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<td>---</td>
<td>4.6</td>
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<td>369±28</td>
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[a] Dry weight of silica relative to volume of solvent. [b] Conducted in pure water [c] Determined from thermogravimetric analysis (TGA) assuming that the incombustible residues were SiO₂. [d] Determined from intensity average diameter of dynamic light scattering (DLS). [e] Determined from number average diameter of electron microscopy images. [f] Determined from intensity average diameter (DLS) of PMMA core particles after removal of silica by alkali treatment. [g] Flocculation (not further characterized).
Fig. 2. SEM (a and c) and TEM (b and the inset) images of silica/PMMA composite particles (a and b) prepared by static dispersion polymerization of MMA with AIBN in the presence of 200 nm silica particles, and the dimpled PMMA particles after removal of silica particles (c and the inset). Each inset shows magnified images. The scale bars are 1 µm (a, b and c), 100 nm (inset b) and 500 nm (inset c).

Fig. 3. Schematic representation of formation mechanism of silica/PMMA composite particles prepared by static dispersion polymerization with AIBN in the presence of 200 nm silica particles.
Fig. 4. SEM (a) and TEM (b and c) images of silica/PMMA composite particles prepared by dispersion polymerization in an aqueous dispersion of 20 nm silica particles. Image (c) is image (b) at a higher magnification. The scale bars are (a) 1 µm, (b) 200 nm and (c) 100 nm.

Fig. 5. SEM images, TEM images (inset) and corresponding schematic representation of composite products consisting of PMMA and silica (200 nm) prepared by dispersion polymerization in static conditions at pH (a) 3.1, (b) 10.1. The scale bars in the insets are 500 nm.
Fig. 6. SEM images and corresponding schematic representation of silica/PMMA (200 nm) composite particles prepared by dispersion polymerization in water in static conditions at pH 7, with silica particle concentrations (a) 3.0, (b) 1.0, (c) 0.3 wt% relative to water. All of the scale bars are 500 nm.