

Surface properties of silica nanoparticles modified with polymers for polymer nanocomposite applications

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Abstract

The surface of silica nanoparticles was modified with poly(ethylene glycol) methacrylate (PEGMA) or poly(propylene glycol) methacrylate (PPGMA) in order to improve the dispersion of nanoparticles in a polymer matrix. Nanosized silica particles were synthesized by the Stöber method with tetraethyl orthosilicate (TEOS). Silica nanoparticles were treated with triethoxyvinylsilane (VTES) as a coupling agent to introduce reactive groups and the PEG or PPG were then grafted onto the particle surface via UV-photopolymerization. Various analytical methods, i.e., scanning electron microscopy (SEM), thermogravimetry (TG), zeta potential measurement, and water vapor adsorption measurement were used to comprehensively characterize the unmodified(pure) and modified silica particles. The SEM images of the pure and modified particles demonstrated that both particles have a spherical shape and a uniform size without agglomeration. The silica particles modified with polymers showed higher weight loss than unmodified silica particles because of the decomposition of the organic polymers grafted onto the particles. The surface modification of silica particles with polymers decreased the zeta potential values of the silica surface. Modified silica particles had lower water vapor adsorption due to the hydrophobic surface property resulting from the polymers grafted onto the silica surface. In addition, we have developed an electrical conductivity measurement as a novel method to analyze the surface properties of silica nanoparticles. The modified silica particles had lower electrical conductivity than that of unmodified silica particles.

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1. Introduction

The functionalization of particle surfaces is one method for tuning the overall properties of particles to fit targeted applications. In recent years, there has been an increased interest in the surface modification of inorganic nanoparticles with organic materials in numerous areas including photocatalysts, sensors, pharmaceuticals, and electronic devices [1–8]. In the fabrication of polymer nanocomposites, the incorporation of silica nanoparticles with an extremely large surface area into polymers improves the polymer mechanical performance significantly [9–11]. However, the dispersion of nanoparticles in the polymer matrix is rather poor due to their incompatibility with the polymers and their large surface-to-

volume ratio. For instance, physical blending of hydrophobic polymers (e.g., polystyrene or polypropylene) with hydrophilic inorganic particles (e.g., silica particles) may lead to phase separation or agglomeration of particles, resulting in poor mechanical, optical, and electrical properties [12]. Furthermore, particles with high surface energy are easily able to agglomerate as the size of the particles decreases [13,14]. To solve these problems and to achieve a uniform dispersion of particles in the polymer matrix, we propose in this study the surface modification of silica nanoparticles with polymers. Although the effect of functional groups on the surface properties of the particles is not yet clearly understood, it is expected that the introduction of polymers on the silica surface will increase the surface hydrophobicity, leading to better dispersion of particles in the polymer matrix.

In this study, the surface modification of silica particles was carried out by a hybrid method using organosilane coupling agents [15–20]. Nanosized silica particles were synthesized by

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the Stöber method and silica particles were then treated with triethoxyvinylsilane (VTES) as a coupling agent to introduce vinyl groups [21,22]. Finally, the surface that was treated with VTES was grafted with poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) via UV-photopolymerization. To investigate the surface properties of unmodified and modified silica particles, scanning electron microscopy (SEM), thermogravimetry (TG), and water vapor adsorption measurement were used. In addition, we developed an electrical conductivity measurement as a novel method to analyze the surface properties of silica nanoparticles.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), VTES, poly(ethylene glycol) methacrylate (PEGMA MW 360 and MW 526) and poly(propylene glycol) methacrylate (PPGMA MW 375) were obtained from Aldrich (USA). 1-Hydroxycyclohexyl phenyl ketone (otherwise known as Igacure[®] 184) was obtained from Ciba Specialty Chemicals (USA). Absolute ethanol and ammonia solution (28 wt.% ammonia) were obtained from Duksan (Korea). All chemicals were used as received without further purification.

2.2. Preparation of the pure silica particles

The spherical silica particles were prepared by the modified Stöber method using TEOS as a precursor [23]. The first solution was a mixture of 16.75 ml TEOS and 133.25 ml ethanol, and the second solution was a mixture of 3.81 ml 28 wt.% ammonia, 40.78 ml deionized water, and 105.46 ml ethanol. Under stirring, the first solution was added to the second solution, so that the total volume of the solution was about 300 ml. The mixture was stirred for 210 min. The final composition was 0.25 M TEOS, 0.188 M ammonia, 8 M water, and 13.6 M ethanol.

2.3. Preparation of the surface-modified silica particles

For the surface modification of silica particles, 2.4×10^{-3} mol VTES was added into the prepared pure silica particle solution, and the reaction was allowed to continue for an additional 19 h with stirring. The particles were then separated by centrifugation and washed with ethanol. The washing process was repeated at least three times. After the washing process, PEGMA360, PEGMA526, or PPGMA were added with an equimolar amount of VTES into each solution which was previously treated with VTES. Igacure[®] 184, as a UV-light sensitive initiator, was added in an amount of 5 wt.% of the monomer. The solution was exposed to UV light (intensity 1000 mW/cm²) for 600 s to induce UV-photopolymerization on the surface of the silica particles. Particles were then washed again. The mechanism of grafting PEG or PPG onto silica nanoparticles via UV-photopolymerization is presented in Fig. 1.

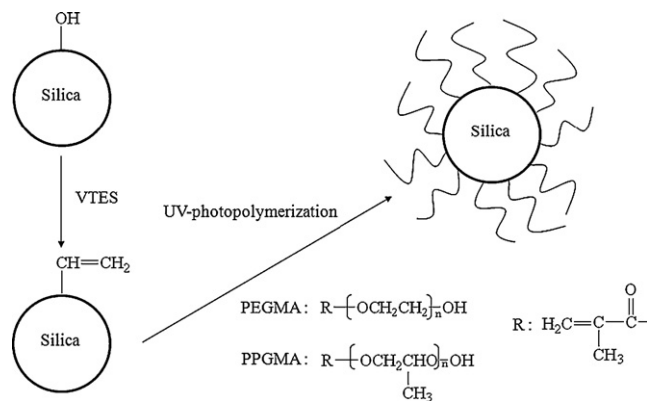


Fig. 1. Grafting of PEG or PPG onto silica nanoparticles by UV-photopolymerization.

2.4. Characterization of the silica particles

The size and shape of silica particles was observed using a Hitachi S-4200 SEM instrument. The SEM sample was prepared by placing a drop of suspension onto a glass plate and then drying under vacuum. Thermogravimetry analysis of silica particles was carried out using a Q-5000IR TG instrument with heating to 500 °C at 50 °C/min to examine the presence and amount of polymers grafted onto the surface of the particles. A Nano ZS Zetasizer (Malvern Instrument Ltd.) was used to determine the zeta potential of the silica particles. The water vapor adsorption measurement was used as one of the methods to compare the surface hydrophobicity of the particles. After drying to a constant weight using H₂SO₄, the particles were allowed to adsorb water vapor in a closed container containing liquid water at 25 °C for 7 days. During the measurement, it was ensured that the particles were not in direct contact with the liquid water. The amount of water vapor adsorbed was estimated by weighing the particles before and after water vapor adsorption. In order to develop a novel method to investigate the silica surface properties, the pure and modified silica particles were dispersed in ethanol and the electric conductivity of the suspension solution was obtained using an impedance analysis Hewlett-Packard 4192 instrument.

3. Results and discussion

3.1. Size and shape

SEM images of the pure and modified silica particles are shown in Fig. 2. These images demonstrate that both pure and modified particles have a uniform size and spherical shape. It was also observed that there was no agglomeration of particles after surface modification. The sizes of pure particles and particles modified with PEGMA526 were 150.7 nm and 174.7 nm, respectively. The average sizes of each particle sample are shown in Table 1. The size of silica particles modified with polymers is slightly larger than that of pure silica particles.

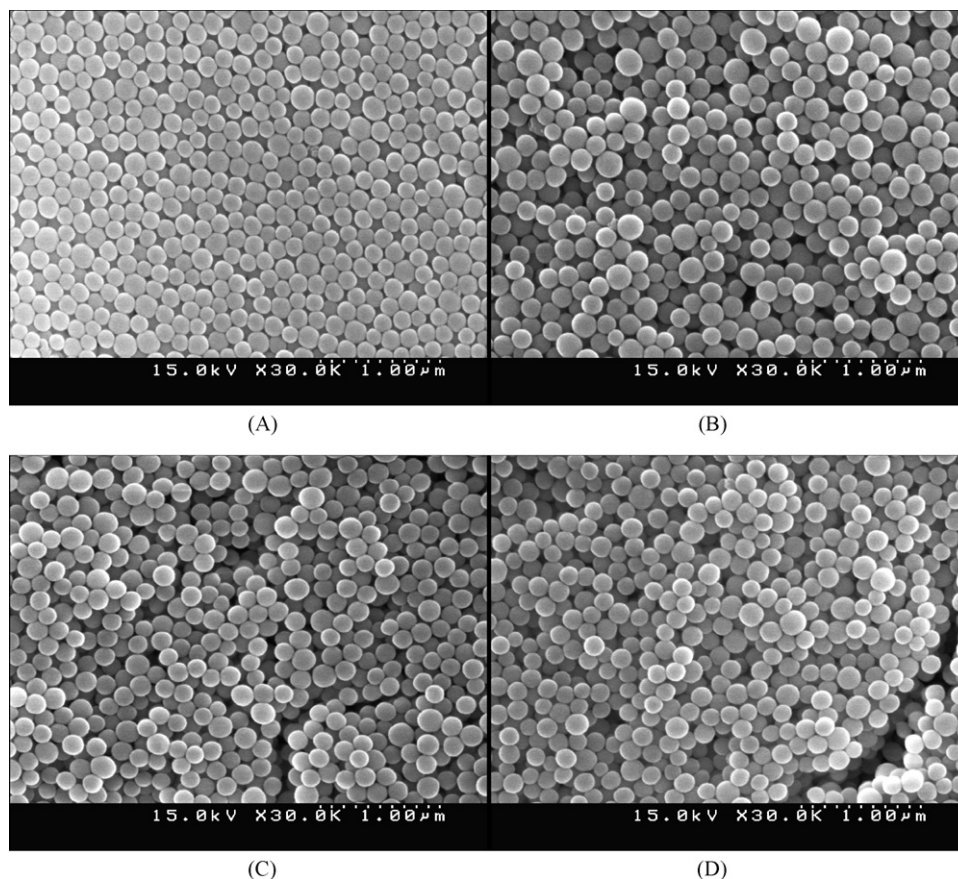


Fig. 2. SEM images of (A) pure silica particles, (B) PEG360 silica particles, (C) PEG526 silica particles, and (D) PPG silica particles.

3.2. Thermogravimetry analysis

The presence and the amount of grafted polymers on the silica surface can be estimated by TG [24]. Fig. 3 shows the weight loss of the silica particles when heated to 500 °C at 50 °C/min. The observed weight loss below 100 °C was due to the evaporation of ethanol and water. A further weight decrease between 100 °C and 500 °C is related to organic group decomposition and silanol group dehydroxylation. Pure silica particles showed a weight loss of 9.4% and silica particles modified with PEGMA526 showed a weight loss of 10.7% at 500 °C. The weight loss of the silica particles is listed in Table 2. These results indicate that the surface of pure silica particles was successfully modified with PEG and PPG, as we proposed. However, we could not observe a significant difference in weight loss according to the type of grafted polymer.

Table 1
Average sizes of pure and modified silica particles

Silica particles	Average size (nm)
Pure silica	150.7 (±17.9)
PEG360 silica	171.2 (±23.4)
PEG526 silica	174.7 (±18.9)
PPG silica	164.8 (±18.0)

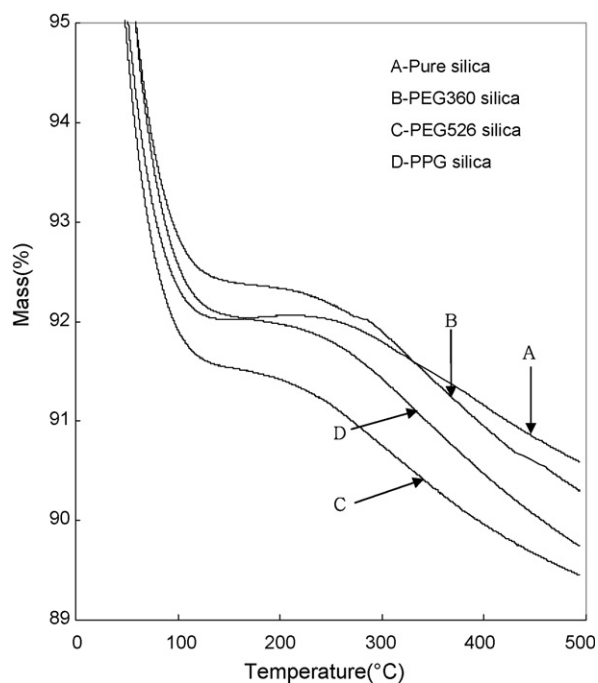


Fig. 3. Weight loss of pure and modified silica particles when heated to 500 °C at 50 °C/min.

Table 2
Weight loss of pure and modified silica particles when heated to 500 °C at 50 °C/min

Silica particles	Weight loss (%)	
	100 °C	500 °C
Pure silica	7.7	9.4
PEG360 silica	7.1	9.7
PEG526 silica	8.1	10.7
PPG silica	7.4	10.3

3.3. Zeta potential measurement

The surface charge properties of silica particles in suspension were determined in terms of the zeta potential. The zeta potential is an important factor controlling the dispersion stability of the silica suspensions, which results in the existence of an energy barrier preventing the proximity of particles [25,26]. When the solution pH is lower than the isoelectric point of silica, hydroxyl groups on the silica particles are deprotonated, producing negative charges on the surface. Since the silanol groups on the silica particles are used as reactive sites in surface modification, there should be fewer silanol groups left on the modified particles than on the pure silica particles. Thus, it is expected that there would be fewer negative charges on the modified particle surface. The zeta potential values of pure and modified silica particles are listed in Table 3. As expected, the modified silica particles exhibited lower zeta potential values than pure silica particles. This confirmed the successful modification of silica particles with the polymers.

3.4. Water vapor adsorption measurement

Fig. 4 presents the amount of water vapor adsorbed on the pure and modified particles. The pure silica particles showed the highest water vapor adsorption (0.195 g/g), while surface-modified silica particles showed lower water vapor adsorption than that of pure silica particles. The hydroxyl groups that the pure silica particles have on their surface make the particle surface hydrophilic. However, the polymer chains replacing hydroxyl groups on the particle surface by modification makes the surface more hydrophobic. Therefore, the amount of adsorbed water on the particle decreased as the surface was modified with polymers. However, we could not observe a significant difference in the amount of water adsorbed according to the type of grafted polymer.

Table 3
Zeta potential of pure and modified silica particles

Silica particles	Zeta potential (mV)
Pure silica	-43.1 (± 1.9)
PEG360 silica	-36.4 (± 3.2)
PEG526 silica	-30.0 (± 0.4)
PPG silica	-42.0 (± 1.9)

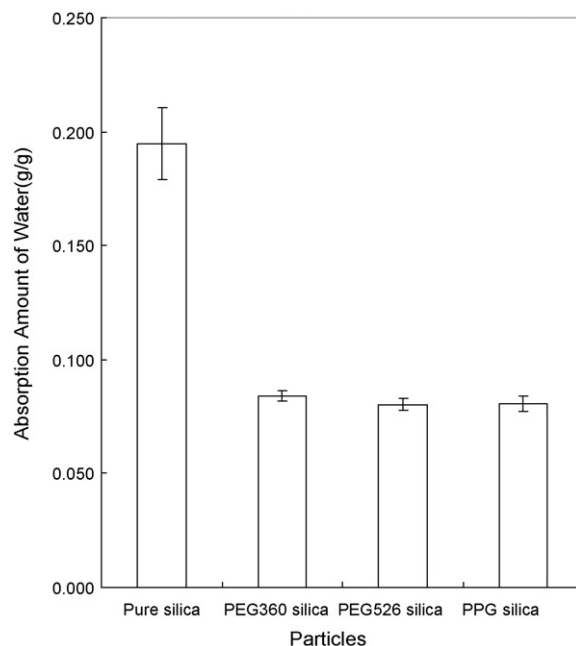


Fig. 4. Comparison of water vapor adsorption of the pure and modified silica particles.

3.5. Electrical conductivity measurement

In order to examine changes in surface properties due to surface modification, we developed an electrical conductivity measurement as a novel analytical method. The electrical conductivity of pure and modified particles is shown in Fig. 5. The surface of pure and modified particles is negatively charged due to the deprotonation of hydroxyl groups, which is consistent with our zeta potential measurement. Thus, addition of negatively charged particles in ethanol increased the electric

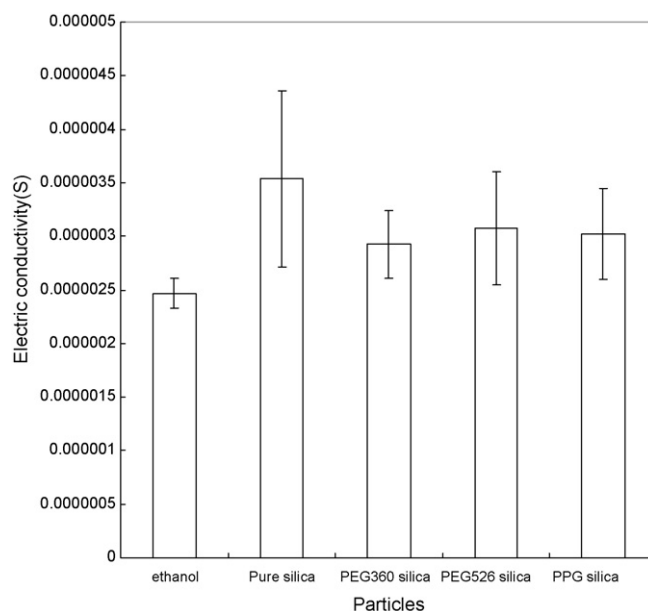


Fig. 5. Comparison of electric conductivity of the pure and modified silica particles when ethanol was used as a solvent.

conductivity of the solution. Note that the electric conductivity was lower for the addition of the modified particles than for pure silica particles since PEG and PPG grafted onto the modified silica surface are non-conductive.

4. Conclusions

Nanosized silica particles were modified with PEG or PPG through UV-photopolymerization. Various analytical methods were used to comprehensively characterize the unmodified and modified silica particles. The surface modification of silica particles changed some properties on the surface, i.e., electric charge and hydrophilic nature. Modified silica particles showed a larger weight loss at 500 °C in TG analysis and a lower zeta potential value than that of unmodified silica particles. The silica particles modified with polymers showed a lower water vapor adsorption than that of pure silica particles due to a more hydrophobic surface. The electrical conductivity measurement which was developed in this study was capable of verifying the surface modification by polymers, since the modified particles had a lower value of electric conductivity than that of pure silica particles. These results indicate that the surface modification of silica particles via UV-photopolymerization with polymers was carried out successfully and that the modification made the silica particle surface more hydrophobic.

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