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Polymer Particles Incorporating ZrO_2 Nanoparticles Prepared by Miniemulsion Polymerization

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Acrylic polymer particles incorporating ZrO_2 nanoparticles (hybrid latex dispersion) were synthesized by miniemulsion polymerization. The refractive index of the films prepared from the hybrid latex increased with increase of ZrO_2 content. Surface-modified ZrO_2 nanoparticles could be dispersed in polymer matrix having phosphoric acid group.

Nanoparticles and polymer materials are of great scientific and industrial interest because of their unique properties. There have been efforts to incorporate nanoparticles into polymer matrices to enhance the functionalities and properties of the materials, since the nanoparticle-dispersed polymer material (polymer/nanoparticle hybrid) has unique properties derived from those of the nanoparticle. For example, nanoparticles of TiO_2 and ZrO_2, which have high refractive index and no absorption in the visible region, have been dispersed in a variety of polymers to obtain optical materials with high refractive index and clarity.[1–5] In general, metal oxide nanoparticles with hydrophilic surfaces are hardly dispersed in organic solvents and polymer matrices. Then the surface modification of the metal oxide nanoparticles with organic functionalities is frequently carried out to achieve their dispersion into polymer matrices. Surface-modified metal oxides, such as TiO_2, can be dispersed homogeneously in polymers and the corresponding monomers.[1–4]

Polymer particles have high surface-to-volume ratio, functional groups at the surface, monodispersity, and simplicity of preparation and are suitable for the support of nanoparticles. The production of hybrid particles by incorporating nanoparticles into polymer particles has been a field of intense research.[6–10] Miniemulsion polymerization is suitable for the incorporation of functional compounds such as dye and nanoparticles into polymer particles.[6] The miniemulsion droplets composed of monomers and nanoparticles are converted to the corresponding polymer particles containing the nanoparticles (hybrid latex particles). Latex dispersion is an important industrial material especially for waterborne coating, and the film formation process has been studied in detail.[11] A void-free polymer film is formed from latex dispersion via the evaporation of water, the packing and deformation of the latex particles, and the healing of the interface by polymer diffusion across the boundary between the adjacent cells (Figure 1-iii), whereas the microstructure derived from the polymer particles could remain in the film. For example, latex particles have surface functional groups such as sulfate, which is derived from the radical initiator and the surfactant used in the emulsion polymerization. The film formation of organic–inorganic hybrid latex particles appears to be more complicated, since the inorganic components such as nanoparticles often aggregate and prevent polymer diffusion.[12] Thus, a complete uniform structure composed of the polymer and the nanoparticle are not achievable in film prepared from hybrid latex. It was reported that the mixture of polymer particles and ceramic nanoparticles forms the film in which the nanoparticles are ordered between the polymer particles.[13]

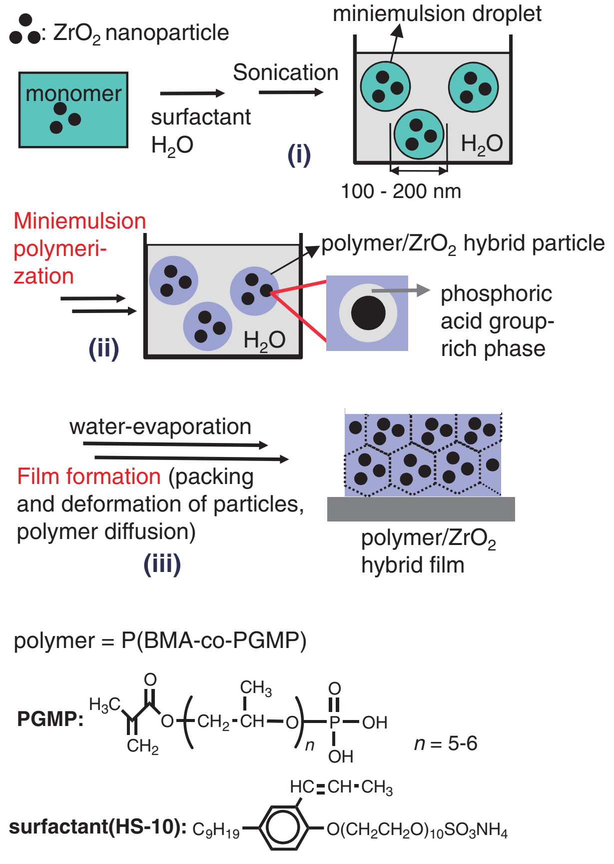

Figure 1. Schematic representation of the preparing hybrid particles and the film formation.

In this paper, we synthesized polymer particles incorporating ZrO_2 nanoparticles (acrylic polymer/ZrO_2 hybrid latex dispersion) by miniemulsion polymerization (Figure 1). Films were prepared from the hybrid latex dispersion, and their optical properties such as transparency and refractive index were evaluated. The compatibility between the polymer and the metal oxide depends on their interface, which plays an important role in the structure and properties of the polymer/metal-oxide hybrid. Metal oxide nanoparticles are expected to be dispersed homogeneously in polymer matrix containing functional groups

Table 1. Optical properties of films prepared from latex

Latex	PGMP /mol %	ZrO_2 /wt %	Haze[a]	n[b]
1a	20	0	0.5	1.473
1b	20	15	0.8	1.477
1c	20	20	0.9	1.488
1d	20	30	1.2	1.492
2	10	24	6.2	1.480
3	5	25	7.2	1.477
4	30	30	3.1	—
5[c]	20	20	2.0	1.489
6	—	15	—	—

[a]Based on data from 380 to 780 nm. [b]Refractive index at 633 nm. [c]BMA:BA = 9:1.

that interact with the surface of the metal oxide nanoparticle.[14] Therefore, polymer containing phosphoric acid groups and surface-modified ZrO_2 nanoparticles were used to disperse ZrO_2 nanoparticles homogeneously in the polymer matrix. We discuss the microstructure and properties of the hybrids and the effect of phosphoric acid toward them.

n-Butyl methacrylate (BMA, Nacalai) and *n*-butyl acrylate (BA, Nacalai) were distilled under reduced pressure prior to use. ZrO_2 nanoparticles of which the surface is modified by methacryl groups (diameter: 10–20 nm, average: 12 nm, dispersed in 2-butanone, Solar Co., Ltd.), poly(propylene glycol) methacrylate phosphate (PGMP, UNI-CHEMICAL Co., Ltd., Figure 1), vinyl phosphonic acid (TCI), HS-10 (Dai-ichi Kogyo Seiyaku, Figure 1), $K_2S_2O_8$ (KPS, Nacalai), and hexadecane (Nacalai) were used as received. Latex dispersions were synthesized by miniemulsion polymerization (Table 1, Supporting Information,[18] and Figure 1). A typical experiment preparing latex is shown below. A 100 mL flask equipped with a condenser and a mechanical stirrer was filled with BMA (2.835 g, 0.02 mol), PGMP (1.9248 g, 0.004 mol, 20 mol % vs. BMA), ZrO_2 (2.05 g, 30 wt % vs. polymer), hexadecane (0.36 g, 1.6 mmol, hydrophobe), HS-10 (0.05 g, 0.06 mmol, surfactant), and water (25 mL). ZrO_2 was dispersed in the mixture of BMA and PGMP before adding to the flask (see below). The mixture was stirred for 15 min and ultrasonicated (Branson 450 digital sonifier) for 9 min in an ice bath to obtain the miniemulsion (Figure 1-i). The miniemulsion was purged with nitrogen gas for 1 h and then heated to 80 °C. An aqueous solution (1 mL) of KPS (0.05 g, 0.19 mmol, radical initiator) and $NaHCO_3$ (0.01 g, 0.13 mmol) was added to the flask, and the mixture was vigorously stirred at 80 °C for 18 h. The obtained emulsion **1d** (22 wt % as estimated by gravimetric analysis) consisted of particles having DLS diameter of 144 nm and a narrow size distribution (polydispersity index: <0.1). The TEM image of **1d** is shown in Supporting Information.[18] The films were cast on Pyrex glass plates, dried slowly at 40 °C, and annealed at 80 °C to remove water inside the film.

Polymer particles incorporating ZrO_2 were synthesized by miniemulsion polymerization using ZrO_2 nanoparticle-dispersed monomer (Figure 1). Methacryl-modified ZrO_2 nanoparticles (2-butanone dispersion) were added to a mixture of BMA and PGMP. After stirring for 30 min, the mixture was a translucent white dispersion, indicating that ZrO_2 nanoparticles are dispersed in the mixture without aggregation or precipitation. Then 2-butanone was removed under reduced pressure to afford the nanoparticle-dispersed monomer BMA/PGMP/ZrO_2. In contrast, the mixtures of BMA/ZrO_2 and BMA/vinyl phosphonic acid/ZrO_2 prepared in a similar way were opaque white dispersion. Acrylic polymer/ZrO_2 hybrid latex dispersions **1b**–**1d** and **2**–**5** were obtained by miniemulsion polymerization (Table 1, Supporting Information[18]). The miniemulsion droplets composed of the nanoparticle-dispersed monomer BMA/PGMP/ZrO_2 would be converted to the hybrid particles (Figure 1-ii). Transmission electron microscopy (TEM) of hybrid particles (**1b**–**1d** and **2**–**5**, Figure 2, Supporting Information[18]) gives direct proof that 10–20-nm-diameter ZrO_2 nanoparticles are incorporated in all polymer particles and placed at the core of the particle. In latex **6**, which was synthesized by use of BMA/ZrO_2, only some of the polymer particles incorporated ZrO_2 nanoparticles. It is considered that the phosphoric acid group of PGMP interacts with the surface of ZrO_2 nanoparticle and is indispensable for incorporating ZrO_2 particles into the miniemulsion droplets of the monomers and their conversion to the polymer particles.

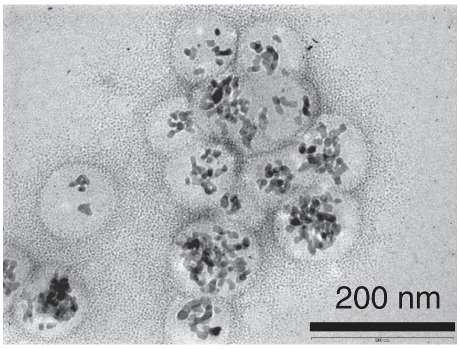

Figure 2. TEM image of polymer/ZrO_2 hybrid particle **1c**.

The films were cast on a glass plate by use of latex dispersion **1a**–**1d** and **2**–**5**, and their UV–vis absorption spectra and refractive index were measured. All films had high transparency (total light transmittance: >90%, Supporting Information[18]). The haze value of the films prepared from **1a**–**1d**, which contain 20 mol % of PGMP, was low (0.5–1.2%) and increased slightly with ZrO_2 content (0–20 wt %, Table 1). The haze values of the films from **2**, **3**, and **4**, which contain 10, 5, and 30 mol % of PGMP, respectively, were higher (6.2, 7.2, and 3.1%) than that of **1d**. In contrast, the film prepared from **6**, which contains no PGMP, was opaque. This shows that polymer/ZrO_2 hybrid containing the appropriate concentration of phosphoric acid group forms a transparent film, in which the light scattering due to ZrO_2 nanoparticle is minimal. The films containing an excess or insufficient concentration of phosphoric acid group are not transparent due to their higher light scattering. The refractive index of the hybrid films prepared from latex dispersion **1b**–**1d** increased with increase of ZrO_2 content (Table 1 and Figure 3).[15] The films prepared from the hybrid latex containing less PGMP (**2** and **3**) had a smaller refractive index than **1c**, although ZrO_2 content of **2** and **3** is higher than that of **1c**. The refractive index of film from **4**, which contains 30 mol % of PGMP, could not be measured. These results indicate that, in the film formation from polymer/ZrO_2 hybrid particle (Figure 1-iii), ZrO_2 nanoparticles neither prevent poly-

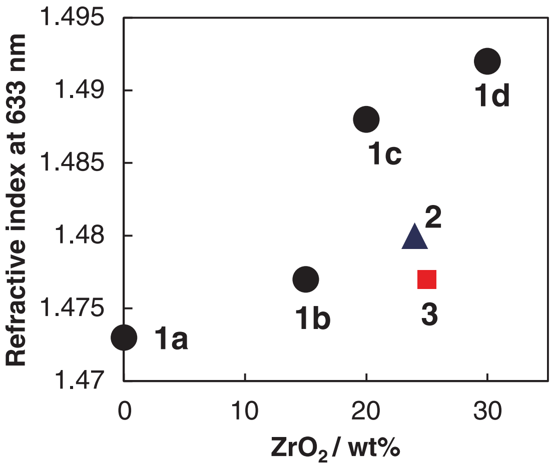

Figure 3. Hybrid film refractive index as a function of ZrO_2 content.

mer diffusion nor aggregate and then a void-free film is formed. ZrO_2 nanoparticles would be surrounded by the phosphoric acid group-rich phase and be dispersed in the polymer matrix to increase the refractive index. In **2** and **3**, it is thought that part of the ZrO_2 nanoparticles aggregate due to the insufficient concentration of phosphoric acid group and result in decreasing the refractive index and also increasing the haze value as described above. The excess concentration of the phosphoric acid group in **4** could cause the phase separation between the acryl polymer chain and the phosphoric acid group, which can induce the light scattering and increase the haze value. The refractive index of the film from **5** was almost the same as that of **1c**, whereas the glass transition temperature (T_g) of the polymer component of **5** (estimated T_g of P[BMA-co-BA]: 10 °C) is lower than that of **1c** (T_g of PBMA: 30 °C).[17] The films from **1b**–**1d** were annealed at 120 °C for 1 h, but the refractive indexes of the films were the same before and after the annealing. These results also show that, in the film formation of **1b**–**1d** (at 40 °C), polymer diffusion of PBMA results in forming a void-free film (Figure 1-iii) and does not affect the refractive index.

In summary, uniform and transparent polymer/ZrO_2 hybrid film was formed from the hybrid latex particles. Surface-modified ZrO_2 nanoparticles are dispersed in the polymer matrix uniformly with the aid of the phosphoric acid groups to increase the refractive index. The refractive index of the films increased with increase of ZrO_2 content, which could be applied to adjust the refractive index of waterborne coating.

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15 The refractive index of the hybrid film prepared from **1b**–**1d** is lower than the values calculated by the Lorentz–Lorenz equation (ref 16) assuming that ZrO_2 is dispersed in P[BMA-co-PGMP],

$$(n^2 - 1)/(n^2 + 2) = \Sigma\, v_i(n_i^2 - 1)/(n_i^2 + 2) \qquad (1)$$

where n is the refractive index of the hybrid film, v_i and n_i are the volume fraction and refractive index of component i, respectively. For example, the refractive indexes of **1d** are 1.492 (measured) and 1.516 (calculated). The refractive indexes of ZrO_2 and P[BMA-co-PGMP] were 2.148 (ref 2) and 1.473 were employed, respectively. This indicates that the dispersion of ZrO_2 nanoparticles in the polymer matrix is not perfectly uniform and ZrO_2 nanoparticles potentially aggregate in part, whereas all the hybrid films have high transparency as described above.

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18 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.