Preparation of Nanocomposite Microspheres Containing High Concentration of TiO_2 Nanoparticles via Bead Mill Dispersion in Organic Solvent

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TiO_2 nanocomposite microspheres with a high concentration of around 40 mass % were successfully prepared. TiO_2 nanoparticles were well dispersed in butyl acetate by a bead mill. After adding an acrylic monomer and initiator, the suspension was heated at 80 °C for 16 h to evaporate butyl acetate and polymerize the monomer. The replacement of butyl acetate with the monomer as the dispersion medium was effective in producing a high concentration of TiO_2 nanocomposite microspheres.

Optical films such as light diffusion films, antireflection films, and prism sheets are indispensable for liquid crystal displays. Light diffusion films are usually produced by the deposition of highly refractive and transparent polymer microspheres on resin films. There is an upper limit to the refractive index of commercial organic polymers (1.4–1.5); therefore, incorporation of high-refractive-index materials such as TiO_2 nanoparticles into microspheres is an effective method to enhance the refractive index. To produce highly refractive microspheres, a large amount of TiO_2 nanoparticles should be incorporated into a monomer. However, incorporation of TiO_2 nanoparticles reduces the transparency of microspheres. To overcome this problem, nanoparticles must be dispersed at the nanometer level. It is difficult to directly disperse a high concentration of TiO_2 nanoparticles (above 20 mass %) in a monomer, because such a high-concentration suspension usually has high viscosity.[1] In a previous study, we found that replacement of the dispersion medium was very effective in the production of films with a high concentration of nanoparticles.[2] In this process, a bead mill was used to disperse TiO_2 nanoparticles by mechanical stress in an organic solvent at the nanometer level. After adding a monomer and polymerization initiator, the suspension was heated to evaporate the organic solvent and polymerize the monomer. When neopentyl glycol dimethacrylate was used as the monomer, it was found that the resulting polymer film contained 38 mass % TiO_2 nanoparticles and had a high refractive index of 1.8.[2] Several researchers have also produced polymer films with a high concentration of nanoparticles;[3,4] however, microspheres with a high concentration of nanoparticles have not yet been prepared. In this study, we produced microspheres with a high concentration of TiO_2 nanoparticles by the replacement process.

Ten mass % TiO_2 nanoparticles (MT150W, Tayca, primary diameter: 15 nm), butyl acetate (Wako Pure Chemicals), and a dispersant (Solsperse32000, Lubrizol) were pumped into a bead mill (UAM150, Kotobuki Industries) filled with fine zirconia beads (diameter: 50 μm). The peripheral speed of the rotor in the centrifugation section was 10 m/s. The diameter of nanoparticles was measured by a particle analyzer (FPAR-1000, Otsuka Electronics Co., Ltd.). Figure 1 shows the time dependence of the dispersion of TiO_2 nanoparticles in butyl acetate. The dispersed particle diameter of TiO_2 nanoparticles reduced rapidly in the initial stage and was minimum (47.8 nm) at a dispersion time of 280 min. However, it increased thereafter owing to reagglomeration. The turbidity (NTU) of the suspension was measured by a turbidity meter (HI93703, Hanna Instruments Ltd.) after diluting the suspension with pure butyl acetate. The turbidity of butyl acetate containing TiO_2 nanoparticles with a diameter of 47.8 nm at 280 min was 2688 NTU; however, the turbidity of the suspension at 10 min was 18256 NTU. Thus, the smaller the diameter of the dispersed TiO_2 nanoparticles, the higher was the transparency of the suspension (Figure 2). The dispersibility of TiO_2 nanoparticles in butyl acetate was determined by using a transmission electron microscope (TEM) (JEM-3000F, JEOL Ltd.). Figure 3 shows TEM images of the TiO_2 nanoparticles before and after dispersion. It was confirmed that TiO_2 nanoparticles were well dispersed after bead mill dispersion.

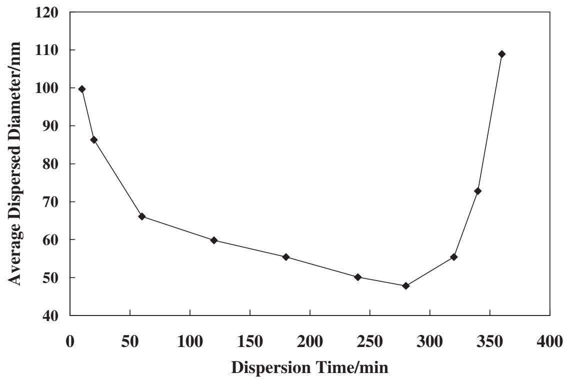

Figure 1. Time dependence of bead mill dispersion of TiO_2 nanoparticles in butyl acetate.

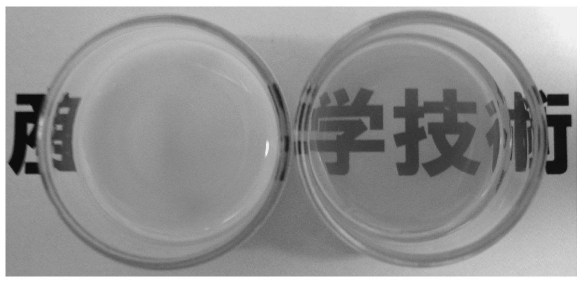

Figure 2. Turbidity of butyl acetate containing a dispersion of TiO_2 nanoparticles at bead mill dispersion times of 10 (left) and 280 min (right).

To produce microspheres with a high concentration of TiO_2 nanoparticles, neopentyl glycol dimethacrylate (monomer,

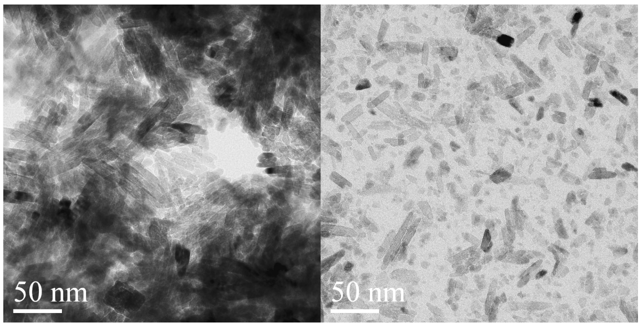

Figure 3. TEM images of TiO_2 nanoparticles before (left) and after (right) bead mill dispersion for 280 min.

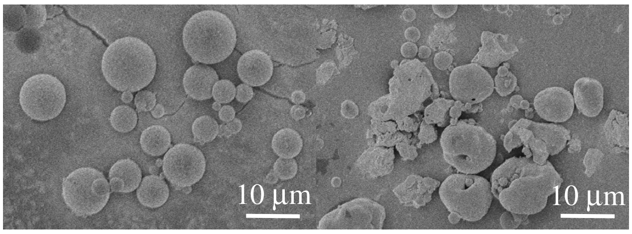

Figure 4. SEM images of composite polymers containing a dispersion of TiO_2 nanoparticles (left) and an aggregation of TiO_2 nanoparticles (right).

1.44 g) and benzoyl peroxide (initiator, 0.2 g) were added to butyl acetate (16.0 g) containing a dispersion of TiO_2 nanoparticles. Two types of butyl acetate containing TiO_2 nanoparticles with different dispersibilities were used: one contained nanoparticles with a small diameter (47.8 nm), and the other contained aggregated TiO_2 nanoparticles (above 100 nm). They were suspended in 5 mass % aqueous poly(vinyl alcohol) solution at 500–800 rpm for 2 h. Then, they were heated at 80 °C for more than 16 h to evaporate butyl acetate and polymerize the monomers.

The morphologies of the composite polymers were observed by using a scanning electron microscope (SEM) (JSM-6340F, JEOL Ltd.). Figure 4 shows SEM images of the polymers containing TiO_2 nanoparticles. The suspension containing nanoparticles with a small diameter was polymerized successfully; they were microspheres. In the case of the aggregated TiO_2 nanoparticles, they were not microspheres. Aggregated TiO_2 nanoparticles prevented the formation of microspheres. Hence, the dispersibility of TiO_2 nanoparticles in a suspension is important not only for producing transparent microspheres but also for forming microspheres.

The TiO_2 concentration in the composite polymers was determined by a differential thermal analyzer (TG8120, Rigaku). The TiO_2 concentration was defined by the residual weight after the sample was heated up to 1000 °C under O_2 atmosphere. The TiO_2 concentrations of these two kinds of composite polymers were 39.3 (dispersed TiO_2) and 39.8 mass % (aggregated TiO_2). The measured TiO_2 concentrations in the polymers were almost the same as the initially calculated concentrations. This result indicates that butyl acetate evaporated and that almost all the TiO_2 nanoparticles transferred into a monomer phase. Therefore, replacement of the dispersion medium is effective in the production of polymer materials with a high concentration of TiO_2 nanoparticles.

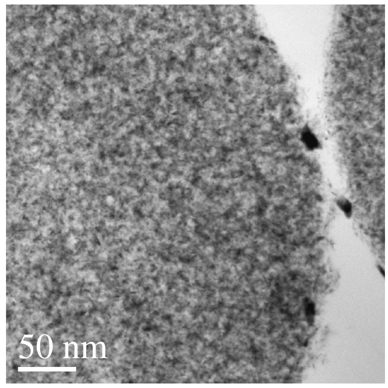

Figure 5. Cross-sectional TEM image of a microsphere in which TiO_2 nanoparticles are close packed and well dispersed.

Figure 5 shows a cross-sectional TEM image of a microsphere containing well-dispersed TiO_2 nanoparticles. The sample was prepared by focused ion beam (FB-2000A, Hitachi Ltd.) after embedding the microspheres in an epoxy resin; its thickness was around 100 nm. TiO_2 nanoparticles were close packed in the microsphere without any vacancies (Figure 5). In a previous study, we prepared a microsphere containing 10 mass % TiO_2 nanoparticles with many vacancies via direct dispersion of the nanoparticles in neopentyl glycol dimethacrylate.[1] In this process, the vacancies were trapped inside the monomer during polymerization because of monomers' high viscosity (5 mPa s at 25 °C). However, in the replacement process, the vacancies moved easily and disappeared with the evaporation of butyl acetate, because it has a low viscosity (0.65 mPa s at 25 °C).

In summary, TiO_2 nanocomposite microspheres with a high concentration of around 40 mass % were successfully prepared. The nanoparticles were close packed and well dispersed in the microsphere without any vacancies. Replacement of the dispersion medium is effective in the production of such microspheres. It is also important to disperse TiO_2 nanoparticles at the nanometer level by means of a bead mill.

This study was conducted at the Hiroshima Prefectural Institute of Industrial Science and Technology.

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