High-concentration Transparent TiO₂ Nanocomposite Films Prepared from TiO₂ Nanoslurry Dispersed by Using Bead Mill

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We developed TiO₂-dispersed nanocomposite polymer films, which have a high concentration of 65 wt. % TiO₂, high refractive index of 1.85, and high transmittance of 81.5% (thickness: 5 μm). Finely dispersed TiO₂ nanoslurry was obtained by using a bead mill filled with fine beads, where two monomers (either neopentyl glycol dimethacrylate or divinylbenzene) and a single organic solvent (butylacetate) were used as a disperse medium. Up to 20 wt. % TiO₂ could be added into a polymer film by the direct dispersion of TiO₂ in the monomer. Furthermore, it was possible to incorporate high-concentration TiO₂ (above 60 wt. %) in the polymer film by replacing the disperse medium with the monomer after the dispersion of TiO₂ in the organic solvent. Visually, the surface of these films was smoother than that of other films prepared by direct dispersion. Further, these films were transparent and had a high refractive index.

KEY WORDS: Nanocomposite Film / Refractive Index / Titanium Oxide / Nanoparticle Dispersion / Disperse Medium Replacement /

Optical films such as anti-reflection films, prism sheets, and diffusion films are utilized in liquid crystal displays (LCDs). Diffusion films play the important role of diffusing the light from the dots to the plane. For achieving greater light diffusion, a film usually requires a high refractive index and transparency. Further, in order to produce polymers with high refractive indices, it is extremely effective to incorporate aromatics, halogens (without F), and sulfur into the structure units of monomers. Monomers such as styrene have a relatively high refractive index (approximately 1.6) because of their benzene structure. Further, fluorine monomers produced and sold by Osaka Gas Chemicals Co., Ltd., have a high refractive index of 1.63; these monomers are based on bisphenol and bisalcohol. However, the refractive indices of such commercial monomers have upper limits.

Many studies have been performed in this field to improve the refractive index of polymer. For example, a refractive polymer, which was designed on the basis of the monomer structure, has been reported.^{1,2} However, it is extremely difficult to synthesize a polymer with a high refractive index from only polymer materials. Consequently, for achieving optimum cost performance, it is suitable to use affordable polymer materials such as the original commercial ones. Recently, nanoparticles such as TiO₂ have been incorporated in organic polymers in order to produce nanocomposite materials. L. Zimmennann *et al.* reported that the incorporation of PbS nanoparticles into gelatin or poly(ethylene oxide) significantly affects the overall refractive index of the nanocomposite materials.^{3,4} Further, B. Wang *et al.* reported that any material prepared from polyarylether(sulfone) solvents containing SiO₂-TiO₂-ZrO₂ has a refractive index of 1.60–1.76.⁵

In order to produce a composite polymer with a high refractive index, it is necessary to incorporate a significant amount of TiO₂. Polymers incorporating TiO₂ with wt. %

greater than 80 have been previously reported.^{6,7} TiO₂ in these polymers was synthesized by hydrolysis such as the sol-gel method. The sol-gel method is useful to synthesize nanoparticles and incorporate them directly into the polymer without agglomeration. However, from the viewpoint of industrialization, the dispersion of nanopowders in solvents is a better method. In the sol-gel method, there are only a few types of nanopowders that can be incorporated because of the lack of many types of precursors. On the other hand, in the dispersion of nanopowders in monomers, many types of inorganic nanoparticles can be incorporated into polymers if only the dispersant and disperse medium are suitable for dispersion.

It is also essential that such optical materials are transparent. Particle agglomeration significantly deteriorates the transparency of nanocomposite materials. Inkyo *et al.* achieved the dispersion of TiO₂ in water up to a primary diameter by using a bead mill filled with fine zirconia beads and obtained a transparent TiO₂-dispersed suspension.^{8,9} However, to prepare nanocomposite materials, the transparent nanoparticle-dispersed monomers are more suitable. Transparent TiO₂-dispersed acrylic monomers were prepared in our previous study in which TiO₂ up to 10 wt. % was dispersed by using a bead mill.¹⁰ This result indicates that there is a possibility of synthesizing transparent nanocomposite materials from transparent TiO₂-dispersed monomers.

In this study, TiO₂-dispersed nanocomposite films were prepared. TiO₂ nanopowders (up to 20 wt. %) have been dispersed directly in monomers such as neopentyl glycol dimethacrylate or divinylbenzene. In contrast, TiO₂ nanopowder was first dispersed in an organic solvent, and then, the replacement of the organic solvent with the monomer yielded nanocomposite films with high TiO₂ concentration (above 60 wt. %) and helped in increasing the refractive index.

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Figure 1. Time dependence of the dispersions of TiO₂ in the different disperse media (◆: monomer A, ■: monomer B, ▲: butylacetate).

EXPERIMENTAL

Materials

TiO₂ (TAYCA, MT-150W), which has a primary diameter of 15 nm and a needle-like rutile crystal structure, was used as an inorganic nanoparticle without any prior treatment. Neopentyl glycol dimethacrylate (monomer A, Hitachi Chemical) and divinylbenzene (monomer B, Wako Pure Chemical Industries) were used as monomers. In this experiment, the polymers of monomers A and B were denoted as polymer A and B, respectively. Butylacetate was used as the organic solvent for the replacement of the disperse medium. Solsperse (Lubrizol Japan Ltd.), which was a polymeric dispersant based on polyesters including the amino group, was used as a dispersant during the dispersion using the bead mill.

Preparation of Slurry

A bead mill (Kotobuki Industries Co., Ltd.) filled with fine zirconia beads (50 μ m in diameter) was used for the nanoparticle dispersion. The nanoparticle, dispersant, and disperse medium (the total amount of materials used was 300 g.) were pumped into a bead mill at a flowrate of 4 mL/s. The peripheral speed of the rotor in the centrifugation section was usually at 12 m/s. The monomer or organic solvent (butylacetate) was used as the disperse medium.

The dispersibility and particle size distribution of TiO₂ in the slurry were measured by using FPAR-1000 (Otsuka Electronics Co., Ltd.) based on the dynamic light scattering theory and the cumulant method.

The turbidity (NTU) of the slurry was measured by using HI93703 (Hanna Instruments Ltd.) after diluting the slurry with a pure solvent.

Film Preparation

TiO₂-dispersed monomers were spin-coated (200–500 rpm) on a glass plate after the addition of 5 wt. % benzoyl peroxide

(BPO), which acts as the initiator. The TiO₂-dispersed monomers coated on the glass plate were polymerized under N₂ atmosphere at 80–100 °C for more than 16 h.

In order to prepare high-concentration TiO₂ films, the monomer (A or B) and the initiator (5 wt. % based on the amount of monomers) were added in TiO₂-dispersed butylacetate. The obtained slurry was spin-coated on a glass plate and was heated at 100–120 °C for more than 16 h in order to evaporate butylacetate and to polymerize the monomer.

Film Evaluation

The refractive index and thickness of films were measured with a prism coupler 2010 (Metricron) using a 633-nm He-Ne laser, where the thickness of samples was 5–8 μ m.

The transmittance (400–780 nm wavelength) of the films was measured by using V670 (JASCO Corporation) with an integrating sphere (ISN-723). Further, transmittance was calculated at a film thickness of 5 μ m.

The TiO₂ concentration was measured by using TG8120 (Rigaku) when heating from room temperature to 1000 °C at 20 °C/min under O₂ at a flowrate of 50 mL/min. The TiO₂ concentration was defined by the residual weight.

The morphology of the film was observed by a transmission electron microscope (TEM) (JEOL Ltd. JEM-3000F, 297 kV) and a scanning electron microscope (SEM) (JEOL Ltd. JSM-6340F). In order to observe a planar view of the film, the focused ion beam (FIB) (Hitachi, Ltd. FB-2000A) was used.

RESULTS AND DISCUSSION

Dispersion of TiO₂ Nanopowder

About 10–15 wt. % TiO₂ was dispersed using 60 wt. % dispersant based on the amount of TiO₂. Figure 1 shows the time dependence of the dispersion of 10 wt. % TiO₂ in slurries. The average diameters of the dispersed TiO₂ reduced dramatically during the early period and then increased again as a result of the reagglomeration of TiO₂ nanoparticles. The

Figure 2. Particle size distributions of TiO₂ in butylacetate at different dispersing time.

Figure 3. TEM images of TiO₂ nanoparticle before and after dispersion at the smallest average dispersed diameter (a: before dispersion, b: after dispersion in monomer A, c: after dispersion in butylacetate).

smallest diameter of the dispersed TiO₂ in monomer B (40.7 nm) was smaller than that in monomer A (46.7 nm). The viscosity of monomer B (1 cP at 25 °C) was lower than that of monomer A (5 cP at 25 °C); therefore, the dispersion of TiO₂ in monomer B was easier than in monomer A. Figure 1 also shows the time dependence of the dispersion of 10 wt. % TiO₂ in butylacetate under the same condition. The viscosity of butylacetate (0.65 cP at 25 °C) is the lowest of all the disperse media used in this experiment. Therefore, the smallest dispersed diameter (37.3 nm) was obtained much earlier. Figure 2 shows the particle size distribution of TiO₂ in butylacetate at different dispersing times. A sharp particle distribution was obtained through the bead mill dispersion. Figure 3 shows the TEM images of the TiO₂ nanoparticle before and after the dispersion in monomer A and butylacetate. TiO₂ was agglomerated before the dispersion as shown in Figure 3a, and a few aggregates of TiO₂ were partly observed, however, it almost dispersed up to the primary diameter as shown in Figure 3b, 3c.

The smallest dispersed diameters and turbidities are showed in Table I. Because of low viscosity, the dispersed diameter in butylacetate was the smallest in the other monomers with 10 wt. % TiO₂. Hence, the turbidity of TiO₂-dispersed butylacetate was the lowest in the TiO₂-dispersed monomers.

Table I. Dispersed diameter and turbidity of TiO₂-dispersed slurries

Disperse medium	TiO ₂ concentration (wt. %)	Dispersed diameter (nm)	Turbidity (NTU)
Monomer A	5	45.6	2524
	10	46.7	3692
	15	51.6	8170
Monomer B	5	42.4	1086
	10	40.7	3074
	15	44.6	5034
Butylacetate	10	37.3	2134

Considering only the monomers, TiO₂-dispersed monomer B had a smaller dispersed diameter and a lower turbidity than those of TiO₂-dispersed monomer A for any TiO₂ concentrations. The more the TiO₂ concentration increased, the higher was the turbidity. However, the tendency of the smallest dispersed diameters was different. The reason is because the transparency is affected by the amount of the dispersed particle greater than the dispersibility of the particle.

The optimum condition of the dispersant for nanoparticle dispersion should be considered; however, in this experiment, the same amount of similar dispersants was added at each dispersion for the purpose of evaluating the same conditions for the following optical measurement.

TiO₂-dispersed Films via Direct Dispersion

The Refractive indices and transmittances of TiO₂-dispersed polymer films were measured after polymerizing the TiO₂-dispersed monomer prepared as discussed in previous section. The dispersed TiO₂ diameter in the films for the measurement was 50 ± 2 nm.

Table II shows real TiO₂ concentrations in films measured

Table II. TiO₂ concentration in films

Polymer	TiO ₂ concentration (wt. %)	
	Calculated	Measured
Polymer A	0	0
	10	11
	15	16
Polymer B	0	0
	10	13
	15	20

by TG. The concentrations of TiO₂ in polymer B were higher than expected. This is because monomer B is more volatile than monomer A. Figure 4 shows the refractive indices and transmittances of TiO₂-dispersed polymer films at various TiO₂ concentrations. Additionally, Figure 5 shows the transmittance in the range of 400–780 nm. The refractive index of pure polymer B (1.60) was higher than that of pure polymer A (1.48) because the benzene structure was included. Each measured refractive index of the prepared samples (both polymers A and B) gained almost linearly in proportion to the TiO₂ concentration. The transmittance of the TiO₂-dispersed polymer films was lower than that of the polymer film without TiO₂ due to the absorption of TiO₂ (Figure 5). In the case of polymer B, the film was so yellowish that the transmittance was relatively low even if TiO₂ was not incorporated in the film.

As a result, we prepared 16 wt. % TiO₂-dispersed polymer A (refractive index: 1.65, transmittance: 92.6% at 5 μ m) and

Figure 4. Refractive index and average transmittance of TiO₂-dispersed polymer films by direct dispersion (◆: monomer A, ■: monomer B, Straight line: refractive index, Dotted line: Transmittance (400–780 nm) at film thickness of 5 μ m).

Figure 5. All light transmittance of TiO₂-dispersed polymer film in the wavelength range of 400–780 nm (a: polymer A, b: polymer A with 16 wt. % TiO₂, c: polymer B, d: polymer B with 20 wt. % TiO₂).

20 wt. % TiO₂-dispersed polymer B (refractive index: 1.75, transmittance: 87.8% at 5 μ m).

TiO₂-dispersed Films *via* Disperse Medium Replacement

It is difficult to disperse relatively high TiO₂ concentrations (above 20 wt. %) in a solvent due to the high viscosity under bead mill dispersion. To counter this, the TiO₂ nanopowder was dispersed in the organic solvent by means of bead mill and then the monomer such as monomer A or B was added in this slurry. Finally, disperse medium was replaced from organic solvent to monomer by evaporating the organic solvent.

Butylacetate was used as the organic solvent for its low viscosity, high volatility, and high solubility in a monomer (monomers A and B). In previous section, 10 wt. % TiO₂-dispersed butylacetate was prepared. The average diameter of the dispersed TiO₂ in the slurry was 50 ± 2 nm for the following replacement and coat. These TiO₂-dispersed films have a smoother surface than the other films prepared by direct dispersion described in previous section. The low viscosity of the slurry probably resulted in a smoother film.

Table III shows that measured TiO₂ concentrations were higher than expected. It is believed that butylacetate evaporated during dispersion and then the TiO₂ concentration was enriched in the slurry. In addition to evaporating butylacetate, monomer B is more volatile than monomer A, as mentioned in previous section. Therefore, the measured TiO₂ concentrations of the polymer B film were considerably higher. Figure 6 shows the TEM images of 7 wt. % and 65 wt. % TiO₂ states in polymer B films. While TiO₂ was well-dispersed in the 7 wt. % TiO₂-dispersed film, TiO₂ was close-packed in the 65 wt. % TiO₂-dispersed film.

Table III also shows the amount of TiO₂-dispersed butylacetate added at the coat and the thickness of films. Theoretically, the evaporation of butylacetate should be greater with a greater amount of TiO₂-dispersed butylacetate. Therefore, the film could become thinner gradually in proportion to

Table III. Properties of TiO₂-dispersed films

Polymer	TiO ₂ concentration (wt. %)		Thickness (μ m)	TiO ₂ -dispersed butyl acetate (wt. %)
	Calculated	Measured		
Polymer A	0	0	5.0 ± 0.4	—
	10	12	5.5 ± 0.5	54.3
	30	38	4.9 ± 0.9	85.2
Polymer B	0	0	5.8 ± 0.3	—
	1	7	7.4 ± 0.3	8.9
	5	20	7.9 ± 0.7	28.1
	10	55	7.7 ± 0.7	54.3
	40	65	7.0 ± 0.9	91.7

Figure 6. TEM images of TiO₂-dispersed polymer B films.

the amount of increase in butylacetate. However, the thickness of any film was almost the same despite identical coating conditions. This is probably because the TiO₂ concentration was too high to tightly bind the monomer units and it decreased the density of the polymer.

Figure 7 shows the refractive indices and transmittances of TiO₂-dispersed polymer films at various TiO₂ concentrations after replacing the disperse medium. Basically, the refractive index increased with the TiO₂ concentration. The highest refractive indices of TiO₂-dispersed polymers A and B were 1.80 (at 38 wt. %) and 1.85 (at 65 wt. %), respectively. For a TiO₂ concentration greater than approximately 20 wt. %, the

Figure 7. Refractive index and average transmittance of TiO₂-dispersed polymer films *via* disperse medium replacement (◆: monomer A, ■: monomer B, Straight line: refractive index, Dotted line: Transmittance (400–780 nm) at film thickness of 5 μ m).

Figure 8. Picture of 65 wt.% TiO₂-dispersed polymer B (Average film thickness: 7.0 μ m) coated on glass plate.

refractive index of TiO₂-dispersed polymer B was lower than that of polymer A. This is because the amount of polymer B in the film was too low in the high-concentration TiO₂ film due to the evaporation of monomer B. In addition, when the TiO₂ concentration in the film was much higher, the concentration of the adhesive dispersant around the TiO₂ particle was also higher. The refractive index of the dispersant (1.46) was lower than that of polymer B (1.60). Hence, the refractive index of the composite film was more significantly influenced by the dispersant than polymer B.

TiO₂-dispersed polymer A films have a high transmittance (above 90%). TiO₂-dispersed polymer B films also have a relatively high transmittance (above 80%), despite high TiO₂ concentrations (above 60 wt.%). The picture of 65 wt.% transparent TiO₂-dispersed polymer B film was showed at Figure 8. In addition, these transmittances were higher than TiO₂-dispersed films prepared by the direct dispersion (Figure 4). This is probably because the TiO₂-dispersed film was smoother. The surface states of TiO₂-dispersed films were showed at Figure 9. The surface of TiO₂-dispersed film prepared *via* disperse medium replacement was smoother compared with that prepared by direct dispersion.

As a result, we prepared TiO₂-dispersed nanocomposite films that had a refractive index of 1.85 and transmittance of 81.5% (polymer B) and a refractive index of 1.80 and transmittance of 91.5% (polymer A). This method could apply to another composite film if butylacetate solubilized with other monomers.

CONCLUSION

We were able to prepare a TiO₂-dispersed polymer B film with a high concentration of 65 wt.% TiO₂, a high refractive

Figure 9. SEM images of cross-sectional TiO₂-dispersed polymer films (a: direct dispersion with 15 wt.% TiO₂, b: disperse medium replacement with 65 wt.% TiO₂).

index of 1.85, and a high transmittance of 81.5%. In the case of monomer A, we prepared 38 wt.% TiO₂ polymer A film (refractive index: 1.80, transmittance: 91.5%). In this study, following two processes are important points.

- 1) Fine TiO₂-dispersed slurries were prepared by using a bead mill that could finely disperse TiO₂ up to almost primary diameter.
- 2) To prepare nanocomposite polymers with high concentration of TiO₂ (above 60 wt.%), replacement of butylacetate with monomer was the effective method.

Acknowledgment. This work was performed in Hiroshima Prefectural Institute of Industrial and Technology and we are grateful for their assistance.

Received: March 6, 2008

Accepted: April 18, 2008

Published: June 11, 2008

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