Effects of particle form on the angular dependence of transmittance for needle-like TiO$_2$ particle arrayed composite films

Hidetoshi MIYAZAKI,[†] Masato MIYOSHI, Hisao SUZUKI[*] and Toshitaka OTA[**]

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690–8504, Japan

[*]Graduate School of Science and Technology, Shizuoka University, 3–5–1 Johoku, Hamamatsu 432–8561, Japan

[**]Ceramic Research Laboratory, Nagoya Institute of Technology, 10–6–29 Asahigaoka, Tajimi, Gifu 507–0071, Japan

Composite films with an array of needle like TiO$_2$ particles in urethane resin matrix were fabricated by applying AC bias. The resulting composite films showed angular dependence of transmittance in the visible-NIR wavelength range. The angular dependence of transmittance of the film increased with the increase in the aspect ratio of the TiO$_2$ particles. The composite films using needle like TiO$_2$ particles with an aspect ratio of 19 indicated that the transmittance changed by 25.4% between 0 and 60° at a wavelength of 500 nm.

Key-words : TiO$_2$, Needle-like particle, Arraying, Angular dependence, Aspect ratio

1. Introduction

Many energy-efficient window materials have been investigated, including heat mirror materials,[1)–3)] thermochromic materials,[1),4),5)] photochromic materials,[1),6),7)] and angular dependence windows.[8)–13)] These investigations reveal that the level of sunlight transmitted through the window materials is dependent on the environmental conditions; thus, energy efficiency can be improved using these window materials.

Energy efficiency in office rooms can be improved between summer and winter by controlling the transmittance of light angles, as transmittance changes depending on the angle of irradiated light. For example, in Tokyo Japan, the zenith angle at noon at the summer solstice is about 78° and that at the winter solstice is 32°; hence, the incident angle into buildings varies greatly between summer and winter. Thus, there is a great deal of interest in angular selective materials for the development of new windows, which can provide energy-efficient properties to blinds, glazing, and domes. Angularly dependent transmitting films have been widely reported, which were formed by multilayer coatings[8),9)] and Cr-base[10),11)] or Ti-oxide base[12),13)] columnar structure films. In contrast, we have reported fabrication of films with arrayed needle-like TiO$_2$ particles by applying AC bias, and described the transmittance anisotropy in the visible-NIR wavelength region of these materials.[14),15)]

In this article, needle-like TiO$_2$ particles were chosen as fillers because of their large refractive index, urethane resin was employed as matrices because of its high transparency, and we fabricated composite films with arrayed needle like TiO$_2$ particles in the urethane matrix by applying AC bias. To prepare composite films with arrayed needle like TiO$_2$ particles, we referred to the fabrication condition (the AC bias of 1 kHz, ±10 V and the

application time of 1 h because of the condition to array needle-like TiO$_2$ particles sufficiently) in the previous reports.[15)] The angular dependence of transmittance for the resulting composite films was observed, and we evaluated the effects of particle size and aspect ratio of needle-like TiO$_2$ particles on the angular dependence of transmittance.

2. Experimental procedure

Needle-like TiO$_2$ particles with various particle sizes were used as the filler, and liquid urethane polymer (APR M-40; Asahi Kasei Chemicals Corp., Tokyo, Japan), which can be cured by UV irradiation, was used as the matrix. The forms and sizes of the employed TiO$_2$ particles are shown in **Table 1**. The particle of sample 1 was sphere like in form, and the others were needle like in form. The aspect ratios of samples 2–4 are close to each other with a value of about 13, and the particle sizes of those increased with the increase of the sample number. The aspect number of

Table 1. The particle size and the aspect ratio of the employed TiO$_2$ particles

Sample number, sample name (Form, Inc.)	Particle size (Long-axis, μm)	Particle size (Short-axis, μm)	Aspect ratio
1. ET-300 (Sphere, Ishihara)	0.02–0.03	—	~1
2. ST-485SA15 (Needle, Titan-kogyo)	0.10	0.008	12.50
3. FT-1000 (Needle, Ishihara)	1.68	0.13	12.92
4. FTL-200 (Needle, Ishihara)	2.86	0.21	13.62
5. FTL-300 (Needle, Ishihara)	5.15	0.27	19.07

Ishihara: Ishihara Sangyo, Osaka, Japan.
Titan-kogyo: Titan kogyo Ltd., Osaka, Japan.

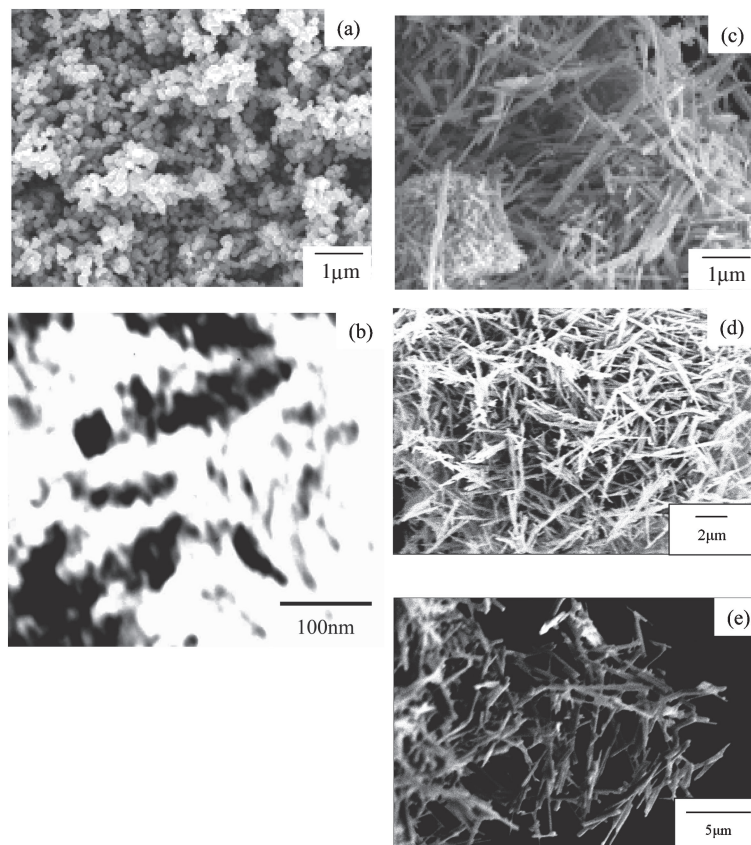[†] Corresponding author: H. Miyazaki; E-mail: miya@riko.shimane-u.ac.jp

Fig. 1. SEM images of source particles of sample 1 (a), sample 3 (c), sample 4 (d), sample 5 (e), and a TEM image of source particles of (b) sample 2.
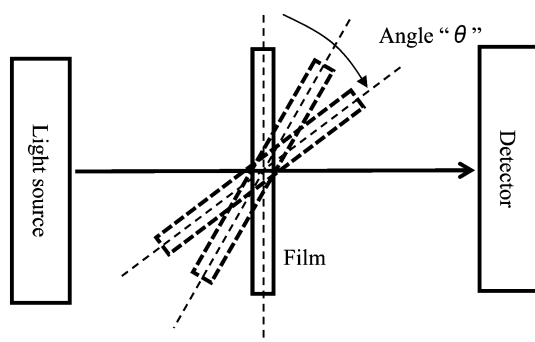

Fig. 2. Schematic illustration of evaluation for an angular dependence of transmittance of a composite film.

sample 5 was much larger than samples 1–4, and the value was about 19. The morphology of the source particles is shown in **Figs. 1**(a)–1(e). The composites were prepared as follows. The liquid polymer, TiO$_2$ particles and ethanol (to lower the viscosity of the resin) were mixed at TiO$_2$ mixing ratios of 0.3 vol %. The mixture was degassed under a pressure of 1 kPa for 1 h to expel the dissolved air introduced during the mixing process. The mixed precursor slurry was placed between flat ITO glasses (with a sheet resistance of about 10 ohm/square), controlling the precursor film thickness to 80 μm. These procedures were conducted in a dark room to prevent exposure of the precursor film to room light. Electrical bias was then applied to the precursor composite at 1 kHz (square wave) with a bias voltage of ±10 V using a universal source (HP-3245A; Agilent Technologies, Santa Clara, CA). After applying bias to the precursor
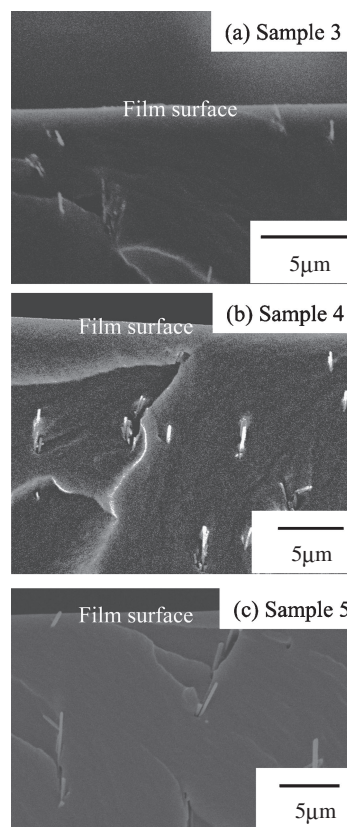

Fig. 3. SEM images of the cross section of the resulting composite films using the TiO$_2$ particles of sample 3 (a), sample 4 (b) and sample 5 (c).
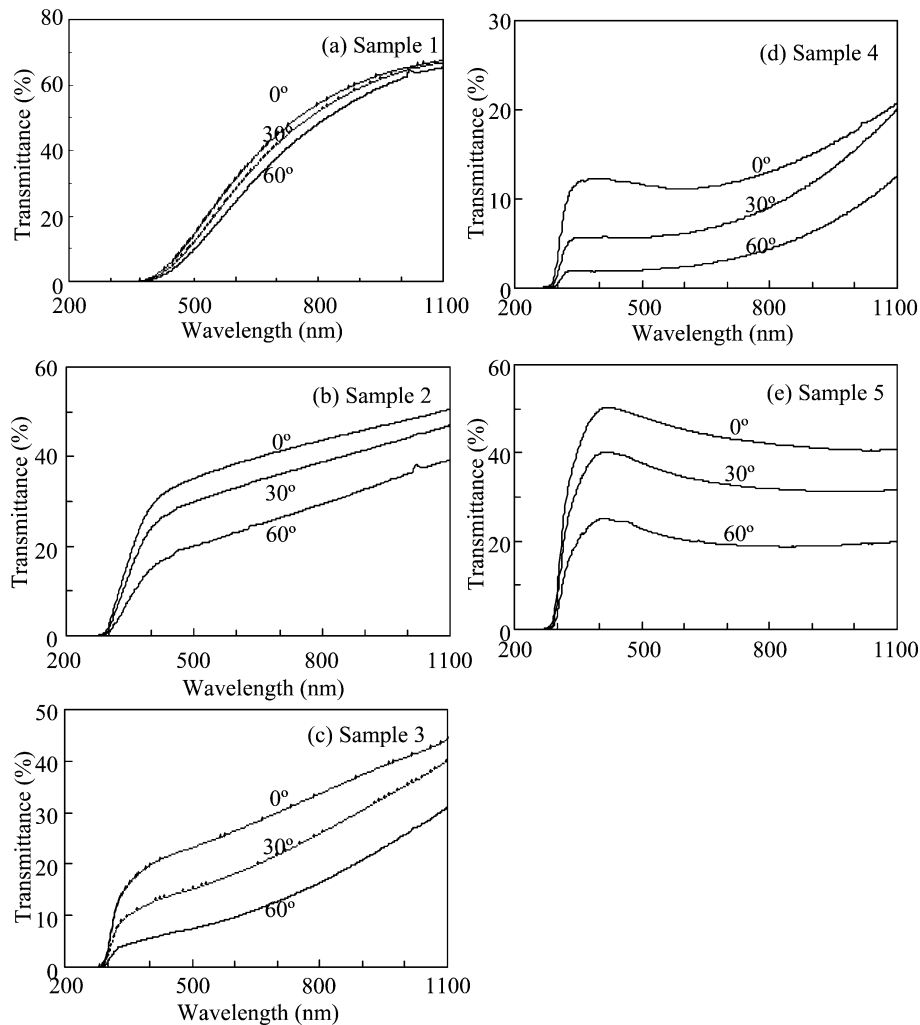
Fig. 4. Transmittance for composite films at various incident angles, and the films using the TiO_2 particles of sample 1 (a), sample 2 (b), sample 3 (c), sample 4 (d) and sample 5 (e).

composite, the composite was cured by irradiation with a 1-kW low-pressure Hg lamp (UV–visible light) and TiO_2–urethane polymer composite films were obtained. The resulting composite film was removed from the ITO glasses.

The source TiO_2 particles were observed by scanning electron microscopy (SEM) (Hitachi S-2100; Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM) (EM-002B; Topcon Corp., Japan). The microstructure of the composite films, which was sliced normal to the film surface, was observed by SEM. The transmittance of the composite films was measured using a Shimadzu UV-1600 spectrophotometer (wavelength range 200–1100 nm) (Shimadzu, Kyoto, Japan). Furthermore, the angular dependence of transmittance was measured from 0 to 60° by rotating the film, where the measured angle was between the direction of irradiated light and a line normal to the composite film surface. The evaluation method of an angular dependence of transmittance for the composite films is shown in **Fig. 2**.

3. Results and discussion

Composite films using the particles of samples 1 to 5 were fabricated, and **Fig. 3** presents cross sectional SEM images of the composite films using TiO_2 fillers of samples 3–5. For sample 2, the particle size was considerably small (less than sub-tens of nanometers), and the particle dispersion in the film could not

be confirmed by SEM and TEM observation. For the films using the TiO_2 particles of samples 3–5, the needle like TiO_2 particles did not aggregate and were dispersed homogeneously in the composite films, confirming that the particles arrayed normally to the film surface. We confirmed the morphology of the films using sample 2; we assumed that the needle like TiO_2 particles arrayed in the film because the film was fabricated with the same fabrication condition as the others.

Composite films using the particles of samples 1–5 were fabricated, and **Figs. 4**(a)–4(e) illustrate the angular dependence of transmittance for the composite films. Measurements of the angular dependence were performed at 15 degree intervals; however, the plots of those were indicated at 30 degree intervals in order for readers to see them clearly.

The composite film using sphere like TiO_2 particles (sample 1, aspect ratio of 1) did not show much angular dependence of transmittance for all wavelength regions [see Fig. 4(a)], and a slight angular dependence of transmittance was observed. The film was tilted from the light irradiated direction in order to measure the angular dependence, and the penetrating distance of light in the film varied; thus, the slight angular dependence of transmittance was observed.

The composite film using needle like TiO_2 particles (samples 2–4, aspect ratio of ~13) showed an angular dependence of
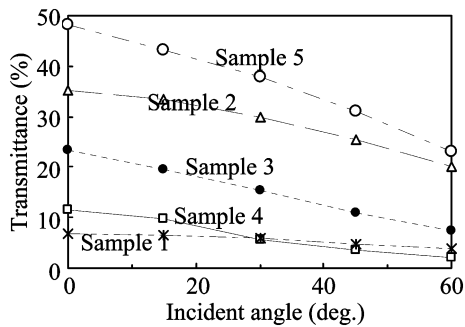
19

Fig. 5. Summarizing the angular dependence of transmittance for the composite films at the wavelength of 500 nm.

transmittance in all wavelength regions, the results of which are shown in Figs. 4(b)–4(d). The composite films using large particle sizes (sample 3, 4, the particle sizes of short axis are 0.13 and 0.21 μm) indicated a broad absorption in the visible light wavelength region, and the results were due to Mie scattering because the filler TiO₂ particle sizes were close to the visible light wavelength. All the composite films exhibited a large degree of angular dependence between 0 and 60° in a wide wavelength region, and the transmittance changed by 9.6–15.8% between 0 and 60° at a wavelength of 500 nm. In contrast, the varying degree of the angular dependence of transmittance was not observed much between each composite film using the TiO₂ fillers of samples 2–4.

Figure 4(e) depicts the angular dependence of transmittance for the composite film using needle like TiO₂ particles of sample 5, aspect ratio of ~19. The spectra at all light incident angles showed broad absorption peaks, and the result was also assumed to be due to Mie scattering. The composite film also exhibited a large degree of angular dependence between 0 and 60° in a wide wavelength region. The transmittance changed by 25.4% between 0 and 60° at a wavelength of 500 nm, and the value was much larger than those (9.5–15.8%) of the films using the TiO₂ fillers of samples 2–4.

Figure 5 shows a summary of the angular dependence of transmittance for the composite films at the wavelength of 500 nm. In summary, increasing the aspect ratio of particles (from 1 to 19) causes an increase in the angular dependence of transmittance for the films. The transmittance of the films using samples 2–4 was different because of Mie scattering, and the details are mentioned above. These results suggest that an energy efficiency window could be designed using the composite films in this investigation, which arrayed the needle like particles with high aspect ratio in the transparent matrix.

4. Conclusion

Composite films with arrayed needle-like TiO₂ particles normal to the film surface were fabricated, and the resulting composite films showed angular dependence of transmittance. The composite films using large particle sizes (close to the visible light wavelength) indicated a broad absorption in the visible light wavelength region due to Mie scattering. When the source particles have the same aspect ratios, the angular dependence of transmittance for films did not vary much, and increasing the aspect ratio of particles caused an increase in the angular dependence of transmittance for the films.

References

1) C. G. Granqvist, *Sol. Energy Mater. Sol. Cells*, **91**, 1529–1598 (2007).
2) E. Shanthi, A. Banerjee, V. Dutta and K. L. Chopra, *J. Appl. Phys.*, **53**, 1615 (1982).
3) C. Jie, G. X. Shi and H. X. Fang, *Sol. Energy Mater. Sol. Cells*, **55**, 323–329 (1998).
4) H. Miyazaki and I. Yasui, *Appl. Surf. Sci.*, **252**, 8367–8370 (2006).
5) I. Takahashi, M. Hibino and T. Kudo, *Jpn. J. Appl. Phys.*, **35**, L438–L440 (1996).
6) W. H. Armistead and S. D. Stookey, *Science*, **144**, 150–154 (1964).
7) J. Scarminio, A. Loureno and A. Gorenstein, *Thin Solid Films*, **302**, 66–70 (1997).
8) J. Karlsson, M. Rubin and A. Roos, *Sol. Energy*, **71**, 23–31 (2001).
9) M. Rubin, R. Powles and K. von Rottka, *Sol. Energy*, **66**, 267–276 (1999).
10) S. Palmer, G. W. Mbise, G. A. Niklasson and C. G. Granqvist, *Sol. Energy Mater. Sol. Cells*, **44**, 297–403 (1996).
11) G. W. Mbise, G. A. Niklasson and C. G. Granqvist, *J. Appl. Phys.*, **77**, 2816–2818 (1995).
12) D. Le Bellac, G. A. Niklasson and C. G. Granqvist, *J. Appl. Phys.*, **77**, 6145–6150 (1995).
13) D. Le Bellac, G. A. Niklasson and C. G. Granqvist, *Thin Solid Films*, **266**, 94–95 (1995).
14) H. Miyazaki, S. Kikitsu, T. Ota and H. Suzuki, *Adv. Powder Technol.*, **22**, 544–547 (2011).
15) H. Miyazaki, M. Miyoshi, T. Otsuka, S. Kikitsu, H. Suzuki and T. Ota, *J. Mater. Sci. Res.*, **1**, 123–127 (2011).