Controlling Transmittance of Visible Light by the Incident Light Angle Using Needle-like TiO$_2$ Particle Arrayed Composite Films

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Abstract
Composite films with an array of needle-like TiO$_2$ particles in urethane resin matrix were fabricated by applying a 1 kHz AC bias with a square wave. In the resulting film, needle-like TiO$_2$ particles were arrayed in the composite films in a direction normal to the film surface. The composite films showed angular dependence of transmittance in the visible-NIR range. For the composite film with arrayed 0.1 vol% TiO$_2$ needle-like particles, the transmittance changed by 16.6% between 0° and 60° at a wavelength of 500 nm.

Keywords: Needle-like particle, Arraying, TiO$_2$, Transmittance, Angular dependence

1. Introduction
Many energy-efficient window materials have been investigated, including heat mirror materials (Granqvist, 2007; Shanthi et al., 1982; Jie C et al., 1998), thermochromic materials (Granqvist, 2007; Miyazaki & Yasui, 2006; Takahashi, I. Hibino & M. Kudo, 1996), and photochromic materials (Granqvist, 2007; Armstead & Stookey, 1964; Scarminio & Gorenstein, 1997). These observations imply that the level of sunlight transmitted through the window materials is dependent on the environmental conditions. Therefore, energy efficiency can be improved using these window materials.

Energy efficiency in an office can be improved between summer and winter by controlling transmittance with light angles, as transmittance changes depending on the angle of irradiated light. Thus, there is a great deal of interest in angular selective materials for the development of new windows, and can provide energy-efficient properties to blinds, glazing, and domes. Angularly dependent transmittance films have been reported, which were formed by multilayer coatings (Karlsson et al., 2001; Rubin & Rottkay, 1999) and Cr-base (Palmer et al., 1996; Wbise et al., 1995) or Ti-oxide base (Bellac et al., 1995, 6145-6151; 94-95) columnar structure films. On the other hand, we have reported fabrication of arrayed needle-like TiO$_2$ particles by applying AC bias with a low frequency of 0.1 Hz, and described the weak transmittance anisotropy in the visible-NIR wavelength region of these materials (Miyazaki et al., 2011; Kikitsu et al., 2011).

In this study, arraying of needle-like TiO$_2$ particles was carried out at high frequency with a square wave. Figure 1 shows a schematic illustration of a sine wave and a square wave. A square wave electric field is more effective for applying a bias to materials than a sine wave. Thus, the arraying of needle-like particles was carried out under a square wave electrical field in the present study. Furthermore, the transmittance anisotropy of the
resulting TiO₂–resin composite film was examined at various incident light angles.

2. Experimental Procedure

Needle-like TiO₂ particles (FT-1000, 1.68 μm length, 0.13 μm in diameter; Ishihara Sangyo, Osaka, Japan) 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. An SEM image of the TiO₂ particles was shown in figure 2. The composites were prepared as follows. The liquid polymer, TiO₂ particles and ethanol (using 0.1 vol% to lower the viscosity of the resin) were mixed at TiO₂ mixing ratios of 0.1 and 0.5 vol%. The mixture was degassed under a pressure of 1 kPa for 1 h to remove 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 Ω/square), controlling the precursor film thickness to 80 μm. These procedures were carried out 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 composite, the composite was cured by irradiation with 1-kW low-pressure Hg lamp (UV-visible light) and TiO₂–urethane polymer composite films were obtained. The resulting composite films were removed from the ITO glasses.

The microstructure of the composite, which was sliced normal to the film surface, was evaluated by scanning electron microscopy (SEM) (Hitachi S-2100; Hitachi, Tokyo, Japan). The optical properties of the composite films were 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° at 10° intervals by rotating the film, where the measured angle was between the direction of irradiated light and a line normal to the composite film surface.

3. Results and Discussion

The composite films were fabricated with a TiO₂ content of 0.5 vol% with application of 1-kHz AC bias for 0, 30, or 60 min. Figure 3 shows SEM images of the composite films fabricated under the conditions described above. For all films, TiO₂ particles did not aggregate and were dispersed homogeneously in the composite films. TiO₂ particles in the composite film without application of bias showed a random array, while those in composite films with bias applied for 30 and 60 min showed slight arraying or arraying of the needle-like particles normal to the film surface, respectively. In a previous investigation (Kikitsu et al., 2011), the arraying of needle-like particles took over 4 h under conditions of AC 10 V, 0.1 Hz, with a sine wave. Therefore, to array needle-like TiO₂ particles, AC bias with high frequency and a square wave was more effective than that at low frequency with a sine wave.

Figure 4 shows the visible-NIR transmittance of the composite films with different film angles from 0° to 60° normal to the irradiated light. For all charts, discontinuous points were observed at 365 nm, and these points represented the change in light source from a tungsten iodide lamp to a D₂ lamp. Little angular dependence of normal to the irradiated light. The inset photographs indicated that the film was (a) placed parallel and (b) tilted 60° from the surface. The film exhibited a large degree of angular dependence between 0° and 60° in the visible light wavelength region. The transmittance changed by 16.6% between 0° and 60° at a wavelength of 500 nm, and this changed by 0.8% between 0° and 60° at a wavelength of 1100 nm.

From the inset photographs in Fig. 5, the letters written on the paper can be seen clearly beyond the film placed parallel to the paper. On the other hand, the letters written on the paper could not be seen beyond the film tilted
60° from the paper. These results also indicated angular dependence in this wavelength region. The refractive indexes \( n_p \) and \( n_s \) of TiO\(_2\) (rutile) are 3.03 and 2.71 at 500 nm, and 2.74 and 2.48 at 1100 nm (Palik, 1997). The refractive indexes in the small wavelength region were higher than those in the large wavelength region. This is because TiO\(_2\) particles cause interaction with the light of shorter wavelength, and the transmittance of the film with an angle of 60° was greater at a wavelength of 500 nm than that at 1100 nm (see Fig. 5).

4. Conclusion

In summary, needle-like TiO\(_2\) particles were arrayed normal to the film surface by applying an AC bias of ±10 V with a square wave to the precursor slurry composite for 1 h. The resulting composite film with arrayed TiO\(_2\) particles showed angular dependence of transmittance. For the film with a TiO\(_2\) content of 0.1%, the transmittance was 20% higher for an angle of 0° to the incident light compared to that for 60°. This study suggested an improvement in the energy efficiency of the material through the angular dependence of transmittance in the visible-near-infrared range.

References


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![Schematic Illustrations](image1.png)

**Figure 1.** Schematic illustrations of (a) a sine wave and (b) a square wave

![SEM Photograph](image2.png)

**Figure 2.** An SEM photograph of Needle-like TiO₂ particles
Figure 3. SEM photographs of the resulting composite films, to which an AC bias of ±10 V was applied before curing for (a) 0 min (no applied bias), (b) 30 min, and (c) 60 min.
Figure 4. Transmittance for composite films at various incident angles where the bias was applied for (a) 0 min, (b) 30 min, and (c) 60 min at film fabrication.
Figure 5. Transmittance for the composite films with TiO$_2$ content of 0.1%. The film was fabricated at 0.1 Hz, square wave, 1 h. The inset photographs show the film (a) placed parallel and (b) tilted by 60° from the paper surface.