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Arraying needle-like TiO_2 particles in a composite film by applying ac bias and its transmittance anisotropy

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ABSTRACT

In an effort to improve energy-efficient windows, we experimented with a precursor slurry composite by using needle-like TiO_2 particles as the filler in a urethane matrix. Applying dc bias to the slurry failed to array the needle-like particles in the composite and to deposit on the film surface because of electrophoretic movement. However, applying ac bias of ±5 V to the precursor slurry composite for 12 h resulted in the needle-like TiO_2 particles being arrayed in the composite in a direction normal to the film surface. This resulted in an improvement in the energy efficiency of the material through an angular dependence of transmittance in the visible–near-infrared range.

1. Introduction

Energy-efficient window materials can control optical transmittance depending on wavelength [1–3], changing temperature (thermochromic materials) [1,4,5] and irradiation light strength (photochromic materials) [1,6,7], which implies that the level of sunlight transmitted through these window materials depend on the environmental conditions. Therefore, energy efficiency can be improved using these types of window materials. The energy-efficient windows are designed as thin films coated on glass sheets or as filler-embedded composites in a transparent resin. We investigated the fabrication of such windows by using composites such as an ITO–resin composite for near-infrared–infrared (NIR–IR) opaque windows [8], a ZnO–resin composite for UV opaque windows [9], a VO_2–resin thermochromic composite [10] and a LaB_6–polymer composite for solar control glazing [11].

Energy efficiency in an office can be improved between summer and winter by controlling transmittance with light angles, as transmittance changes depending on the irradiated light angles. Granqvist and co-workers have reported the development of an angularly dependent material film with columnar structures deposited by sputtering [12,13]. However, the development of an angularly dependent composite material has not yet been reported. By arraying the needle-like particles in a composite, transmittance of light may be controlled using the light angle through this composite. Some previous investigations have reported the fabrication of a material in which needle-like magnetic particles are arrayed using a magnetic field [14,15]. However, all these materials exhibit ferromagnetism, and it is, therefore, impossible to extend this method for non-ferromagnetic materials.

This study aims to fabricate a material in which needle-like particles are arrayed in a transparent resin composite film. The starting materials are needle-like TiO_2 particles as the filler and a liquid urethane resin (photocuring resin) as the matrix. The refractive index of TiO_2 (rutile) is about 2.5 at the wavelength of around 1000 nm, and that of urethane resin is 1.48 at the wavelength of around 1000 nm. A difference between the refractive index of those is large. Thereby, TiO_2 and urethane resin were employed as starting materials. A homogeneous TiO_2–urethane resin composite can be obtained by mixing these precursors and subsequently curing the mixed specimens by irradiation with UV–visible light. To accomplish this, we followed the following process: (1) arraying these needle-like particles by applying bias to the precursor composite slurry, such that the long axis of the particle is oriented in the direction of the applied electrical field (prior to UV–visible light irradiation, the resin is still a liquid); (2) curing the resin by light irradiation to set the arrayed needle-like TiO_2 particles (Fig. 1 illustrates the method of arraying needle-like particles in a composite, and the sketch shows a cross-section of a film) and (3) evaluating the transmittance for the resulting composites at the various irradiated angles.

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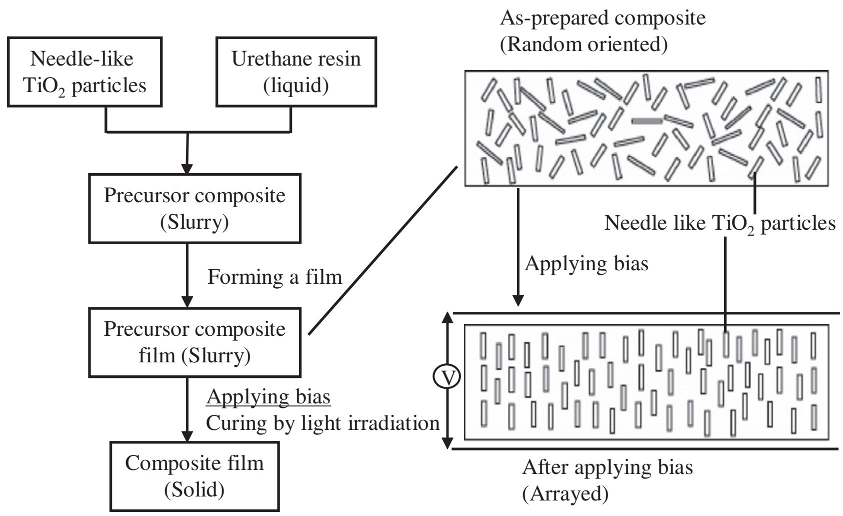

Fig. 1. Schematic illustration of the fabrication method of the composites. (1) Mixing needle-like TiO_2 particles and liquid urethane resin. The mixture is in the slurry state. (2) Painting the slurry between ITO glass substrates, which are transparent electrodes. The film thickness is controlled to 150 μm. The sketch is a cross-section of a precursor film. (3) Applying bias to the slurry precursor film. The needle-like particles are arrayed in the direction of the applied electrical field. (4) Curing the above-mentioned slurry by irradiation of light. The arrayed particles are fixed in the resulting composites.

2. Experimental procedure

The needle-like TiO_2 particles (FT-1000, 1.68 μm length and 0.13 μm 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. The liquid urethane polymer can be cured by irradiation with UV–visible light. A scheme of the composite fabrication is shown in Fig. 1. The composites were prepared as follows. The liquid polymer, TiO_2 particles and ethanol (using 0.1 vol% to lower the viscosity of the resin) were mixed, with the mixing ratio of TiO_2 fixed at 0.3 vol%. The mixture was degassed under a pressure of 100 Pa for 1 h to expel the dissolved air introduced during the mixing process. The mixed precursor slurry was placed between a flat ITO film and coated glass sheets (with a sheet resistance of about 10 Ω/square), controlling the precursor film thickness to 150 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 with dc 10 V or 0.1 Hz and bias voltage of ±5 V using a universal source (Agilent Technology HP-3245A). After applying bias to the precursor composite, the composite was cured by irradiation with UV–visible light and TiO_2–urethane polymer composites were obtained. The resulting composite films were removed from the ITO substrate.

The microstructure of the composite, which was sliced normal to the film surface, was evaluated by scanning electron microscopy (SEM) by using Hitachi S-2100. The optical properties of the composites were measured using a Shimadzu UV-1600 spectrophotometer (wavelength range 300–1100 nm). Furthermore, the angular dependence of transmittance was measured from 0° to 60°, where the measured angle was between the irradiated light direction and the composite film surface.

3. Results and discussion

Fig. 2 shows a cross-sectional SEM photograph of the composite film resulting from the application of 10 V dc bias for 24 h, indicating the TiO_2 particles that migrated to the film surface. The results indicate that the TiO_2 filler was moved to the composite film surface. In general, under an applied electrical field, the particles in a solvent undergo electrophoretic migration because of the force of the electrical field. In this investigation, TiO_2 particles in the precursor composites were moved by the electrical field, and the particles were electrodeposited onto an ITO glass electrode surface. The result clarified that a homogeneous composite cannot be obtained by applying dc bias.

A 5 V ac bias with 0.1 Hz was then applied to the precursor composite films for less than 12 h, and the films were then cured by irradiation with UV–visible light. Fig. 3 depicts the SEM photographs of the cross-sections of the films with the bias applied for 0, 2 and 12 h. In all the films, the filler consisting of TiO_2 particles did not aggregate and was dispersed homogeneously in the composites. In the composites for which the bias was applied for less than 2 h, the directions of the particles were random and out of phase. However, in the composites having an applied bias of 12 h, the directions of the long axis of the particles were oriented normal to the film surface.

Under an applied ac bias, electrophoretic migration of the TiO_2 particles was not observed for any of the conditions. A positive or a negative pole changes periodically under ac bias, and it is assumed that the particles in the precursor composites will move periodically between the upper and the lower sides of the electrodes. The particles in the precursor composites oscillated at regular intervals, preventing them from moving out of the composites.

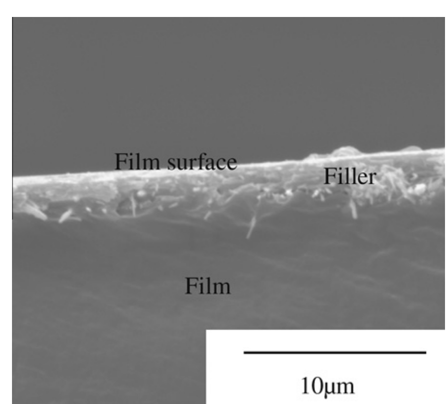

Fig. 2. SEM photograph of the cross-section of the resulting composite film.