

Processing and properties of transparent super-hydrophobic polymer film with low surface electric resistance

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Super-hydrophobic films with low electric resistance were prepared by coating the liquid containing both fluoro-acrylic resin and colloidal silica on an ITO-coated polymer film with the suitable repetition of a one-dimensional groove structure on the surface. The hydrophobicity was effectively enhanced by the roughness mixing effect. The formation of ITO layer on the surface of the base-film decreased the surface electric resistance and improved the durability of the super-hydrophobicity during outdoor exposure. The film prepared in current study satisfies the requirements of transparency, super-hydrophobicity, brightness enhancement property and long lifetime simultaneously. © 2004 Kluwer Academic Publishers

1. Introduction

Films with a water contact angle higher than 150° (i.e., with a super-hydrophobic surface) are currently a subject of great interest and intensive study. The small contact area between water and this type of solid surface is expected to reduce various phenomena such as friction drag and the sticking of snow or water droplets. Hydrophobic properties are well known to be enhanced by an increased surface roughness [1, 2], and super-hydrophobic surfaces require an appropriate surface roughness and low surface energy. Numerous methods to accomplish this have been reported [3].

It is well known that the excellent hydrophobicity of an artificially constructed super-hydrophobic surface gradually degrades over long periods of outdoor exposure. This is the fatal obstacle to be surmounted for the practical application, and one of the causes of this phenomenon is the accumulation of stains that adhere to the surface. Natural super-hydrophobic surfaces such as the surfaces of lotus leaves avoid this problem by continuous metabolism of their surface wax layer, which

makes it possible to maintain hydrophobicity throughout their lifetimes [4–6]. Since the proper metabolic mechanism of a lotus leaf is impossible to duplicate, practical applications of super-hydrophobic surfaces have not been successful.

Recently, we reported that the addition of only a few percent of TiO₂ photocatalyst effectively provides a self-cleaning property to super-hydrophobic films and maintains high contact angles during long periods of outdoor exposure [7]. However, the self-cleaning property of the films depends on the kinetic balance between the decomposition of stain and that of water repellent agent by TiO₂ photocatalyst, and precise material design with considering stains from outer fields is required for successful performance of super-hydrophobic films with TiO₂ photocatalyst. One of the most plausible driving forces for the initial contamination of the surface coated with fluorocarbon is the electrostatic effect, because fluorocarbon is one of the most negative materials in charging series [8]. Once stains stick on a super-hydrophobic surface, more stains accumulate on the

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rough surface. The decrease of static electricity by lowering surface electric resistance to super-hydrophobic films will be one of the fundamental approaches to improve the durability of the hydrophobicity. Whereas, no reports have yet focused on the processing of this type of super-hydrophobic film.

Very recently, we have successfully prepared a super-hydrophobic polymer film with a brightness enhancement property by employing a film with the suitable repetition of a one-dimensional groove structure on the surface of a transparent film material [9]. In this study we have prepared a super-hydrophobic polymer film with a low surface electric resistance through the use of our original process and indium-tin oxide (hereafter denoted as "ITO"), then evaluated its property including durability during outdoor exposure.

2. Experimental

After preparing a solvent by mixing methyl isobutyl keton (Wako Pure chemicals Co., Tokyo, Japan) and butyl acetate (Wako) (45:55 in weight), a commercial fluoro-acrylic resin (FG730B: Central Glass Co., Tokyo, Japan) and a commercial hydrophobic colloidal silica (RX200: Nippon Aerosil Co., Tokyo, Japan) were mixed into the solvent together with a hardening agent (Koroneito HX: Nippon Polyurethane Industry Co., Tokyo, Japan) under sonication. The concentration of total solid content in the liquid was 5% and the ratio of the dry fluoro-acrylic resin, colloidal silica, hardening agent, and mixed solvent was 1.4:1.5:2.1:95. This liquid was employed for the top-coating.

A commercial polymer film with a repeated groove structure designed to enhance the background brightness when observing the film from an angle within about 45° (Brightness Enhancement Film, Sumitomo-3M Co., Tokyo, Japan; hereafter denoted as "BEF") was employed as the starting base-film. ITO layer was formed on the film surface by sputtering method (DC 270 V, 5.6 A, Sputtering pressure: 0.6 Pa, Deposition rate: 18 nm/min) at room temperature. The sheet resistance of the ITO layer obtained was 41 (Ω /square), and its thickness was 160 nm. The prepared liquid was coated on the BEF with ITO layer by spin coating at 1500 rpm for 10 s. Super-hydrophobic polymer films were obtained after drying it for one week at room temperature. For comparison, the same liquid was coated on a commercial polyester (hereafter denoted as "PET") and BEF without ITO under the same condition.

The sessile drop method was used for the contact angle measurement with a commercial contact angle meter (CA-X, Kyowa Interface Science, Japan) and a 3 mg water droplet. The contact angle was measured at five different points. The water sliding angle (the critical angle where a water droplet with a certain weight begins to slide down the inclined plate) was also measured by a commercial sliding angle measurement system (SA-11, Kyowa). The sample surface was blown with ionized air to eliminate the static electricity before each measurement. The microstructure was observed by scanning electron microscopy (SEM: Jeol-6300, Japan Electron Optics Laboratory Co., Tokyo, Japan). Transmittance

of the light in visible wave-length range and haze were evaluated by a spectrophotometer (U-3210, Hitachi Co., Tokyo, Japan) and a haze meter (Haze-Guard Plus, BYK Gardner Co. Columbia, MD, USA). The surface electric resistance on the films was evaluated by a surface resistance tester (Model TR-3, Tokyo Electronics Co., Tokyo, Japan, Electrode distance: 2 cm, Measurement range: 1×10^6 – 1×10^{12} (Ω)). The outdoor exposure test of the films was carried out at the height of 1 m from the ground level in Chigasaki, Kanagawa for 40 days from November to December 2001. Films were set vertical, and the film prepared from the BEF with ITO layer was connected to ground during exposure, then their contact angle change was evaluated.

3. Results and discussion

Water contact angles on the prepared films were summarized in Table I, and SEM microstructures on the films were shown in Figs 1 and 2. The one-directional repeated-groove structure, whose top angle is 90° and groove width is about 50 μ m, was observed on the surface of BEF. Contact angles of PET and BEF were increased by ITO layer formation. The ITO layer formed on the surface of BEF provided very fine roughness. The increase of contact angle due to ITO layer formation is attributable to this microstructure change. Super-hydrophobic films were obtained from both BEF and BEF with ITO after top-coating. The surfaces of the films were coated by hydrophobic colloidal silica—a fluoro-acrylic resin composite homogeneously. The colloidal silica provided a different fine roughness on the surface of the BEF with ITO. No uncoated part was observed. Based on the difference between PET-based films and BEF-based films, it is elucidated that the highly hydrophobic state was attained by combining the roughness of BEF with that of the colloidal silica.

The value of contact angle depended on the measurement direction (parallel and orthogonal against groove structure). The shapes of water droplets on the films from BEF with ITO were shown in Fig. 3. Water droplets elongated to the direction of the groove when contact angle is relatively low. However, the direction dependence was decreased with increasing contact angle. Wenzel modified Young's equation and proposed the following equation to describe the contact angle θ'

TABLE I Water contact angles of prepared films

Base film	ITO layer	Top coat	Measurement direction	Contact angle (deg.)
PET	×	×		59.9 ± 1.3
	×	○		128.8 ± 0.6
	○	×		108.8 ± 0.6
	○	○		126.1 ± 0.5
BEF	×	×	parallel	128.1 ± 0.6
			orthogonal	100.1 ± 0.2
			parallel	158.5 ± 0.4
			orthogonal	157.4 ± 0.5
	×	○	parallel	134.7 ± 0.5
	○	×	orthogonal	117.6 ± 0.9
	○	○	parallel	158.2 ± 0.6
			orthogonal	158.3 ± 0.6

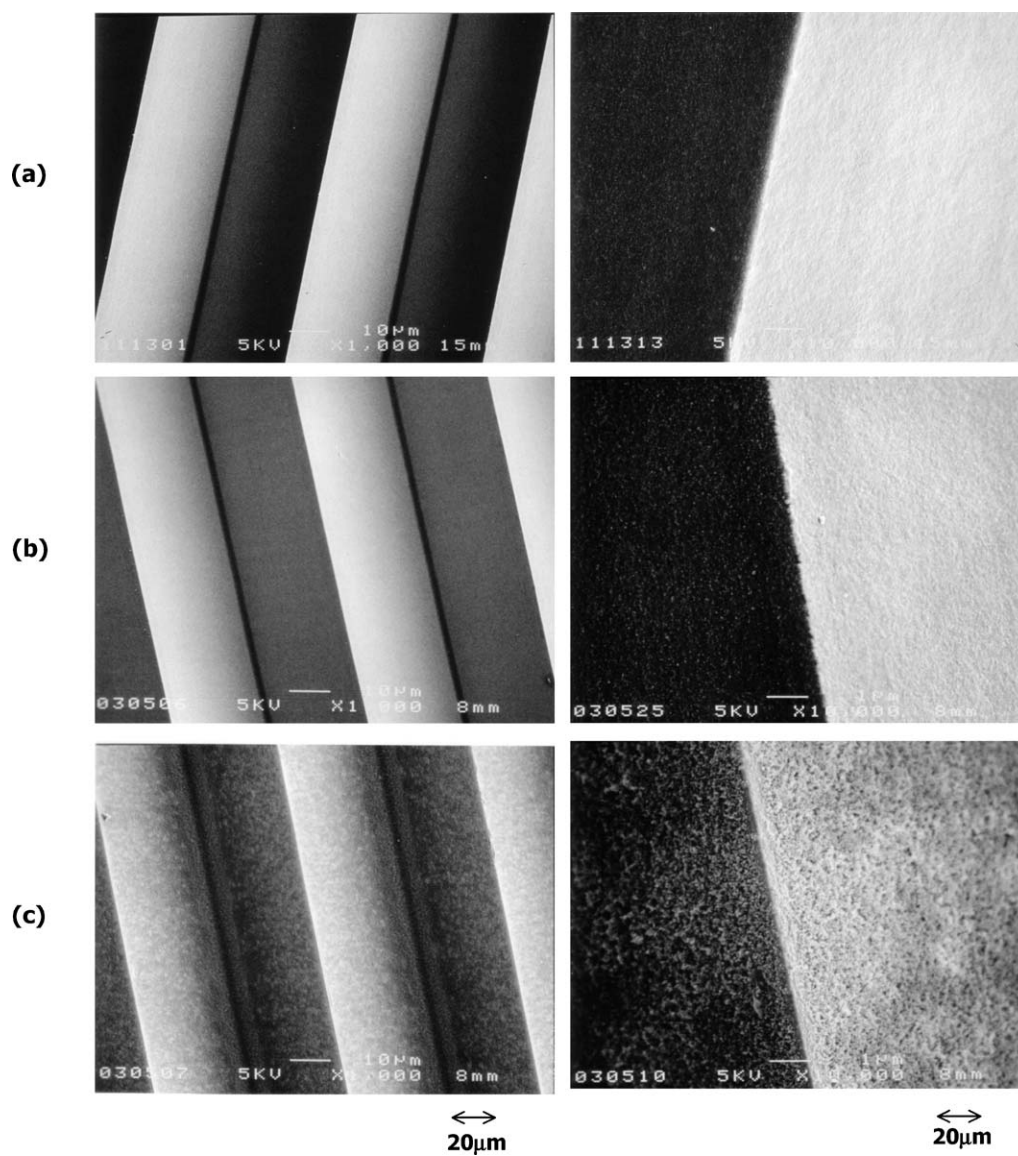


Figure 1 SEM micrographs of prepared films: (a) BEF, (b) BEF with ITO, and (c) BEF with ITO after top coating.

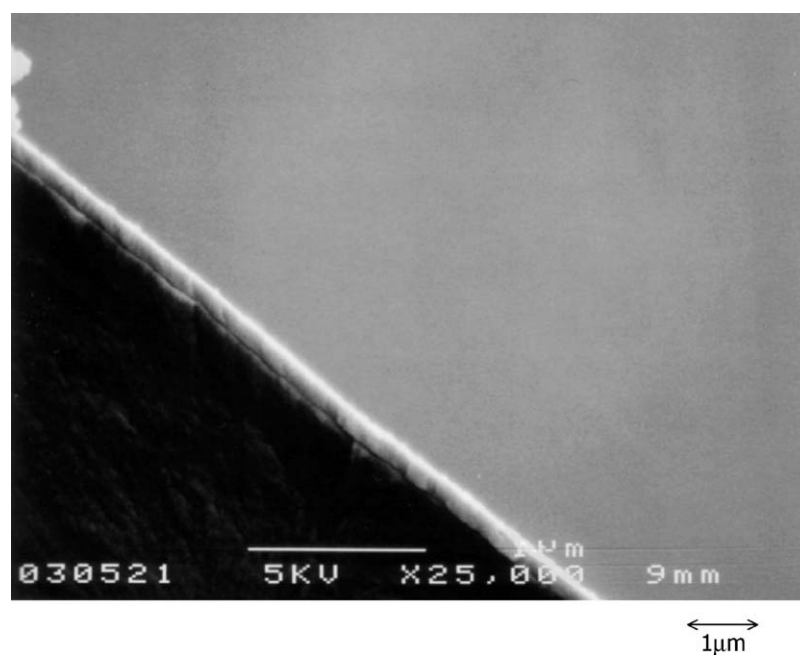


Figure 2 SEM micrographs of the cross section of the BEF with ITO.

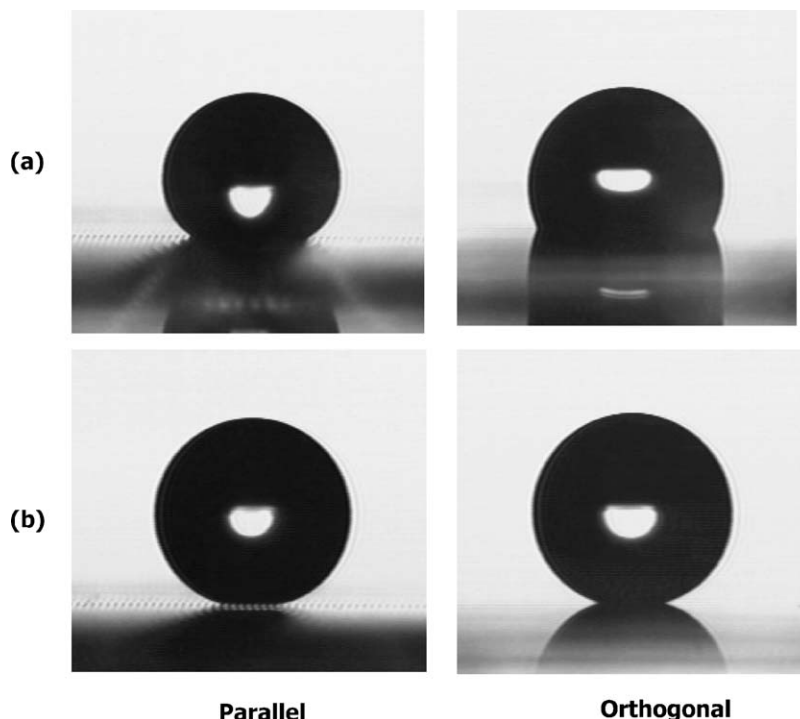


Figure 3 Droplet shapes on the transparent super-hydrophobic film prepared from the BEF with ITO: (a) BEF with ITO and (b) BEF with ITO after top coating.

of a rough surface by considering the increase of the practical surface area [1].

$$\cos \theta' = r(\gamma_{SV} - \gamma_{SL})/\gamma_{LV} = r \cos \theta \quad (1)$$

Here, r is the roughness factor (the ratio of the actual area of a rough surface to the geometric projected area), θ is the contact angle on a flat surface, and γ_{SL} , γ_{SV} , and γ_{LV} are the surface free energies of the solid-liquid, solid-gas, and liquid-gas interfaces, respectively.

When the roughness of a solid surface is large, water does not penetrate into the troughs. Cassie proposed a different equation to describe the contact angle θ' of a hydrophobic rough surface by assuming that the surface is composed of solid and air like a porous material [2]. Since the water contact angle for air can be assumed to be 180° , θ' is described as follows:

$$\cos \theta' = f \cos \theta + (1 - f) \cos 180^\circ = f \cos \theta + f - 1 \quad (2)$$

where f is an area fraction of the solid in unit area. Johnson Jr. and Dettre simulated the contact angle and sliding behavior of a water droplet on an idealized sinusoidal surface [10]. During the regime where Wenzel mode is dominant, they showed that the contact angle and its hysteresis (the difference between the cosine of a receding contact angle and that of an advancing contact angle for a water droplet on a tilted surface) on hydrophobic rough surfaces increase as the roughness factor increases. They also revealed that when the roughness factor exceeds a certain level, the contact angle continues to increase while the hysteresis starts to decrease as a consequence of the switching of the dominant sliding mode from Wenzel's to Cassie's by

the increase of the air fraction at the interface between solid and water. The contact angle hysteresis is known to be proportional to the sliding angle when the deformation of a water droplet at the sliding is constant [11]. Recent studies revealed that the contribution of Cassie's mode is relatively higher than Wenzel's mode for actual super-hydrophobic surface [12, 13]. Fig. 4 shows the direction dependence of the water sliding angle on the super-hydrophobic films from BEF-ITO. Sliding angle was less than 3 degrees in the measurement range, and no direction dependence was observed. It is known that the continuity and the length of three-phase (solid-liquid-air) line is an important factor for the sliding behavior of hydrophobic rough surface [14]. Thus, it is attributed that contact angle was increased and the effect of three-phase contact line was decreased

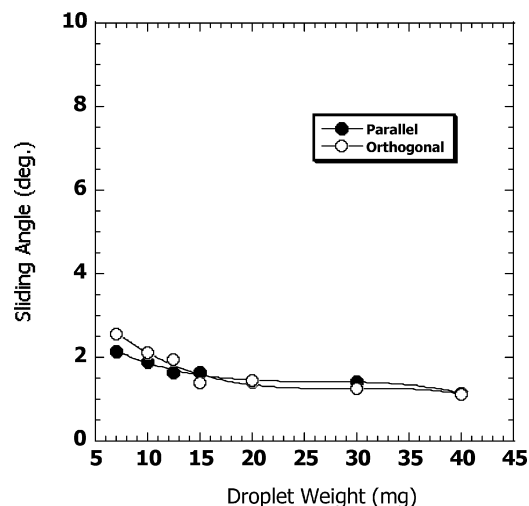


Figure 4 Direction dependence of the water sliding angle on the super-hydrophobic films from BEF-ITO.

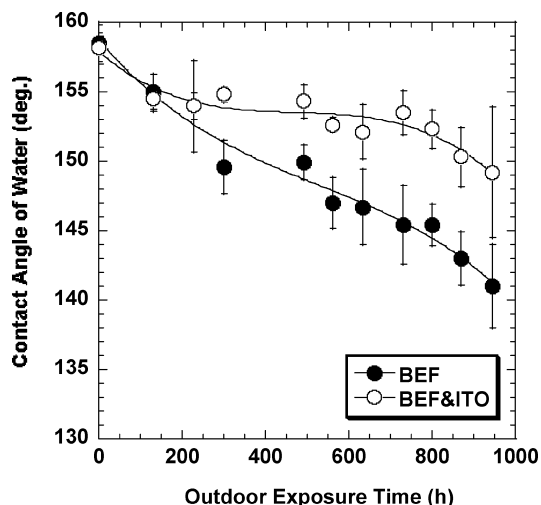


Figure 5 Contact angle change during outdoor exposure.

due to the increase of air intrusion at the interface between solid and water.

The surface electric resistance of the super-hydrophobic film from the BEF with ITO was less than $1 \times 10^6 \Omega$, whereas that from the BEF without ITO was more than $1 \times 10^{12} \Omega$. Fig. 5 shows the comparison of the contact angle change between the films from the BEF with and without ITO during outdoor exposure. Although the initial contact angles were the same between the two, the film from the BEF with ITO sustains higher contact angle than the film from the BEF without ITO. During this experiment, no remarkable microstructural change such as the destruction of top-coating was observed on the films. These results suggest that reducing surface electric resistance is effective for the improvement of the durability of super-hydrophobicity during outdoor exposure.

We have reported that the addition of only a few percent of TiO_2 photocatalyst effectively provides a self-cleaning property to super-hydrophobic films and maintains high contact angles during long periods of outdoor exposure [7]. Although various factors affect the result of outdoor exposure, several mechanisms that might be responsible for the overall self-cleaning performance have been proposed. These include: (1) a long diffusion distance of the radical species on the fluorine-coated surface; (2) effective stain collection to the TiO_2 surface and subsequent photocatalytic decomposition or washing out by water due to the high surface energy or photo-induced hydrophilic property [15] of the surface of TiO_2 ; and (3) reduction of static electricity by the photo-induced hydrophilicity of TiO_2 . It has been confirmed that static electricity on the super-hydrophobic surface with 2.5 wt% TiO_2 photocatalyst was decreased by UV illumination [16]. Results obtained in the current study also support the contribution of the reduction of static electricity to overall self-cleaning performance of super-hydrophobic film with TiO_2 .

Fig. 6 shows transmittance of the visible light for the PET films with and without coatings. This result suggests that visible light transmittance was slightly decreased by ITO layer formation, but was little affected by the top-coating. Haze value measured for

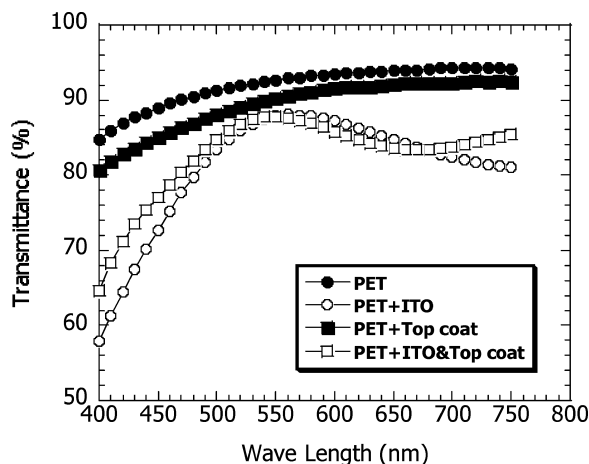


Figure 6 Visible light transmittance of the visible light for the PET films with and without coatings.

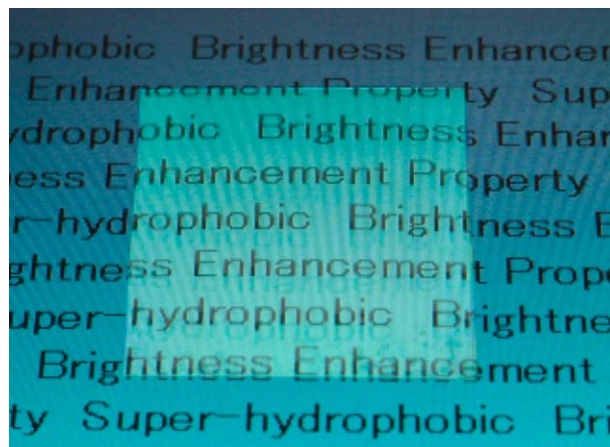


Figure 7 Brightness enhancement effect of the super-hydrophobic film prepared from the BEF with ITO (tilt: 30 deg.).

the PET with top coating was less than 6%. Fig. 7 shows the brightness enhancement property of the super-hydrophobic film through the BEF with ITO. The brightness of the computer monitor was enhanced through the film when the observation angle was about 30° , indicating that this super-hydrophobic film retained the brightness enhancement property of the underlying BEF.

4. Conclusion

In the present study, a super-hydrophobic film with low electric resistance was prepared by coating the liquid containing both fluoro-acrylic resin and colloidal silica on the BEF with ITO. The hydrophobicity was effectively enhanced by the roughness mixing effect. The formation of ITO layer on the surface of the base-film decreased the surface electric resistance and improved the durability of the super-hydrophobicity during outdoor exposure.

The film prepared in this study satisfies the requirements of transparency, super-hydrophobicity, brightness enhancement property and long lifetime simultaneously. This type of film provides a great opportunity for various industrial items with illuminations. The addition of a few percent of TiO_2 photocatalyst to this film will provide longer durability.

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