Preparation of Super-Water-Repellent Alumina Coating Film with High Transparency on Poly(ethylene terephthalate) by the Sol–Gel Method

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(Received May 8, 2000; CL-000434)

Al_2O_3 gel films were prepared on poly(ethylene terephthalate) substrates from Al(O–*sec*-$C_4H_9)_3$ chemically modified with ethyl acetoacetate. A small roughness of about 20–50 nm was found to form on the Al_2O_3 gel films dried at room temperature and then immersed in hot water at 60 °C. When hydrolyzed fluoroalkyltrimethoxysilane was coated on the Al_2O_3 films, transparent thin films with contact angle for water to be more than 150° were obtained.

Wettability of solid surfaces with liquids is governed by the chemical properties and the microstructure of the surfaces. As far as the microstructure of a surface is concerned, fine roughness is well known to enhance the water-repellent and hydrophilic properties.[1–5]

Recently, we have succeeded in forming transparent, super-water-repellent coating films on glass plates through the sol–gel method by the combination of microstructural and chemical approaches; the contact angle for water of the films was 165° and transmittance for the visible light was higher than 92%.[6,7] Al_2O_3 thin films with a roughness of less than 50 nm were formed through immersion of the porous Al_2O_3 films in boiling water after heat-treated at 400 °C. We call this structure the "flowerlike structure." As mentioned above, the heat treatment temperature to obtain the porous Al_2O_3 films was 400 °C in those studies, and thus, the coating films could not be formed on substrates with low thermal stability like polymer substrates. Although transparent super-water-repellent coating films on polymer substrates are required for technological applications, the coating has not been reported so far.

In this paper we have succeeded in preparing transparent, super-water-repellent coating films on poly(ethylene terephthalate) (PET) substrates at low temperatures through the sol–gel method.

Al(O–*sec*-Bu)$_3$ and isopropyl alcohol (*i*-PrOH) were mixed and stirred at room temperature for 1 h. Ethyl acetoacetate (EAcAc) was added to the solution as a chelating agent, and the solution was stirred for 3 h. Water diluted with *i*-PrOH was then carefully added to the solution for hydrolysis and this solution was used for coating. The molar ratio of *i*-PrOH, EAcAc, and H_2O to Al(O–*sec*-Bu)$_3$ was 20, 1, and 4, respectively.

The coating was carried out on PET substrates with a dipping–withdrawing manner (withdrawing speed; 2 mm s^{-1}) in the ambient atmosphere. The coating films obtained were dried at room temperature for 24 h. Then the dried Al_2O_3 gel films were immersed in hot water at 60 °C, and after being dried, heat-treated again at 60 °C for more than 24 h.

Heptadecafluorodecyltrimethoxysilane, which is one of fluoroalkyltrimethoxysilanes (FAS), was used as a water repellent agent. The partially hydrolyzed FAS was coated on the flowerlike Al_2O_3 thin films and then dried at 60 °C for 20 h.

The surface of the coating films was observed with a field emission type scanning electron microscope (FE-SEM, Hitachi S-4500). Thickness of the films was determined through the FE-SEM observation of the cross section of the films. Crystalline phases of the coating films and the powders prepared through the same procedure as the coating films were determined using X-ray diffraction measurements (Rigaku RINT 1100).

Contact angles were measured with a contact angle meter (Kyowa Interface Science, CA-X) at room temperature. Droplets were placed at five positions for one sample and the averaged value was adopted as the contact angle.

Crack-free, transparent Al_2O_3 gel films with a thickness of around 200 nm were obtained on PET substrates. Figure 1 shows the photographs of the surface of the Al_2O_3 film immersed in hot water at 60 °C for (a) 0, (b) 3 and (c) 20 min. The Al_2O_3 gel film without immersion in hot water at 60 °C, (a), shows a very smooth surface. With immersion for 3 min, (b), particles about 20 nm in diameter appear on the surface and thus very small roughness is observed. In the case of immersion for 20 min, (c), the roughness becomes greater, and unevenness with 20 to 50 nm is observed. This structure is very similar to the flowerlike one obtained by immersion of porous Al_2O_3 film heat-treated at 400 °C in boiling water.[6] This shows that the flowerlike structure is also formed on the surface of Al_2O_3 gel film only dried at room temperature and then immersed in hot water at 60 °C.

In FT-IR measurements, chelating bonds between EAcAc and Al atoms were observed in the only dried films, and these bonds were dissociated with the immersion of the gel films in hot water at 60 °C for 1 min. The crystalline phases of the structure formed on the surface of Al_2O_3 gel films with immersion could not be determined by X-ray diffraction measurements for the thin films, because the thickness of the structure was too small. X-ray diffraction pattern of Al_2O_3 gel powders immersed in hot water at 60 °C showed broad peaks due to the boehmite phase. This indicates that the flowerlike structure formed by immersion in hot water at 60 °C consists of boehmite. The boehmite must be formed by the reaction between water and Al_2O_3 gel film, the surface of which dissolves in hot water at 60 °C.

Figure 2 shows the photograph of a water droplet with about 1 mm in diameter on the FAS coated Al_2O_3 thin film with flowerlike structure on a PET substrate. This surface shows extremely high water repellency with contact angle for water of about 150°. UV–visible spectrum of the PET substrates with such a thin film showed a transmittance higher than 90% in the visible range. The contact angle for water on the flowerlike surface without FAS was less than 5°, and the angle on the PET substrates with FAS and on the flowerlike surface with FAS were 110 and 150°, respectively. This shows that the water

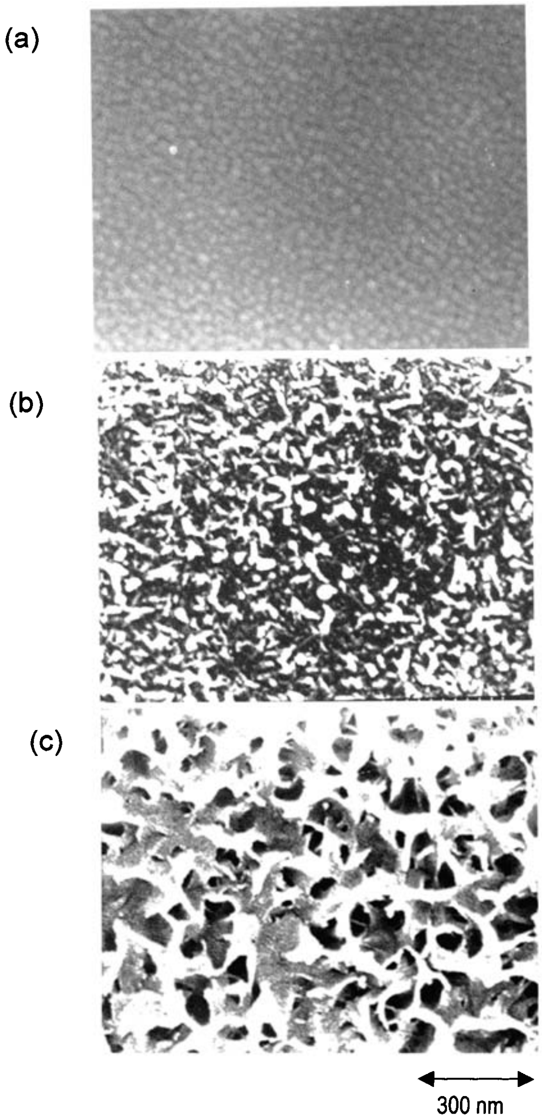

Figure 1. FE-SEM photographs of the surface of Al_2O_3 coating film immersed in hot water at 60 °C for (a) 0, (b) 3 and (c) 20 min.

repellent properties are further enhanced by the roughness with 20 to 50 nm, as can be anticipated.[1]

A peel adhesion tape test to the coating film showed that the coating films strongly adhered to the PET substrates. No cracks were observed on the coating films even if the coated substrates were bent. In addition, the coating films can easily be formed on several kinds of polymers. Thus, the preparation procedure of the coating films in the present study must have high potentiality for practical applications.

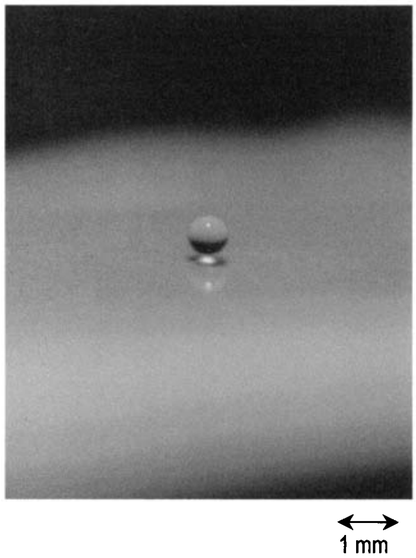

Figure 2. Photograph of water droplet of about 1 mm in diameter on PET with flowerlike Al_2O_3 thin film coated with hydrolyzed FAS.

The present study was supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan.

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