Superhydrophilic Microporous Silica Coatings on Polymer Substrate

Wataru SHIMIZU, Taki MATSUMOTO, Shohei HOSOO, Hitoshi NAGAHIRA and Yasushi MURAKAMI

Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, Tokida, Ueda 386–8567

A transparent smooth superhydrophilic silica coating has been developed by coating a polyethylene terephthalate (PET) substrate with microporous silica and immersing the microporous silica coating in water at 80°C. The microporous precursor sol for coating was synthesized from tetramethoxysilane under neutral conditions by accelerating the rate of the condensation with hydroxyacetone. Immersing the coating in water is an important process for removing not only the methoxy group, but also the hydroxyacetone to form the hydrophilic surface.

[Received August 15, 2007; Accepted October 18, 2007]

Key-words : Superhydrophilic, Microporous silica, Tetramethoxysilane, Non-ionic catalyst, Anti-fog

1. Introduction

An anti-fog coating on a substrate, such as a glass or polymer, is used to keep car windows, bathroom mirrors, camera lenses, eyeglasses and greenhouses from fogging up. Fog is caused when steam condenses on a cool surface and then forms water droplets due to the surface tension of water. Water molecules are more attracted to each other than to air molecules and form a spherical shape. The anti-fog coating material is hydrophobic or superhydrophilic (contact angles of water droplets are less than 5°); the hydrophobic coating repels water to form drops of water which roll on the surface, while on the superhydrophilic coating, the water spreads out without becoming drops of water.

A TiO₂ coating shows a remarkable antifogging effect. Both superhydrophilicity and superoleophilicity are induced on a TiO₂ surface by ultraviolet (UV) irradiation.¹⁾ The TiO₂ coating first needs to be irradiated by UV light for the antifogging effect and does not work for long time in the dark.

Recently, Bico et al. quantitatively discussed the wetting of a solid textured by a designed roughness.²⁾ For a hydrophilic solid substrate, the liquid-solid contact is favored and the hydrophilicity is enhanced by the surface roughness. The liquid is in contact with a rough surface which consists of the solid and pores. Considering both air and liquid with which the pore is filled, the contact angle is described by the following equation,

$$\cos \theta^* = \phi_s \cos \theta_s + (1 - \phi_s) r_a \cos \theta_a + (1 - \phi_s) (1 - r_a) \cos \theta_l \quad (1)$$

where θ^* is the apparent contact angle of the liquid on the rough surface, θ_s is the contact angle of the liquid on the smooth surface of the solid, ϕ_s is the fraction of the base of the liquid drop in contact with the solid, θ_a is the contact angle of the liquid on the air with which the pore is filled ($\theta_a = \pi$), r_a is the fraction of the open cross-section of the pore filled with the air, and θ_l is the contact angle of the liquid on the liquid with which the pore is filled ($\theta_l = 0$). The contact angle can be described by the following equation.

$$\cos \theta^* = (1 - \phi_s) (1 - 2r_a) + \phi_s \cos \theta_s \quad (2)$$

For the porous material, the fraction of the base of the liquid drop in contact with the solid is small. The apparent contact angle of the liquid on the porous material surface decreases with a decrease in the fraction of the top of the pore filled with the air. During the measurement of the contact angle of water, the water is dropped onto the surface in order to fill the pore. r_a in Eq. (2) is then almost zero as

$$\cos \theta^* = 1 - \phi_s (1 - \cos \theta_s) \quad (3)$$

Practically, the entire volume of the pore was not necessarily filled with water under the normal conditions of temperature and humidity.

The volume fraction of the pore filled with water under normal conditions needs to be considered. The multifunctional nanoporous thin films, which exhibit both the superhydrophilic wetting characteristic and a low refractive index, have been fabricated.³⁾ The superhydrophilic porous material involves the pores filled with water, whereas the porous material with a low refractive index involves the pores filled with air.

The adsorption types of water depend on the pore sizes; i.e., the monolayer adsorption of water on the surface of micropores and multilayer adsorption of water on the surface of mesopores. If almost the entire surface of the porous material consists of the inner surface of micropores, only the monolayer adsorption of water occurs and the adsorption strength simply depends on the hydrogen bond strength between a water molecule and an oxygen atom at the inner surface of the micropores.

Hydrophilic coating solutions have been synthesized by adding glycidoxypolytrimethoxysilane (GPS) to the colloidal silica suspensions adjusted to different pHs, with which a PET substrate is coated.⁴⁾ The superhydrophilicity of the coating is developed by the preparation of a coating solution under highly acidic conditions (pH 1 or 2). The glycidoxypoly group remains after the complete hydrolysis of the alkoxy group has occurred.

Microporous coating solutions have never been synthesized from a silicon alkoxide with an ionic catalyst. Under a slight degree of hydrolysis of tetramethoxysilane, the microporous powders are obtained in poor yield.⁵⁾ Competitive reactions forming by-products will be accelerated by the ionic catalyst. An alternative catalyst is required for the preparation of the microporous precursor for coating.

In this study, we demonstrate that the apparently smooth and microporous surface can be readily created below 80°C not from silica nanoparticles or silicon alkylalkoxide, but from silicon alkoxide such as tetramethoxysilane with hydroxyacetone as the non-ionic catalyst under neutral conditions. The superhydrophilic coating on a PET substrate prevents light scattering water droplets from forming on the surface. The antifogging mechanism will be clarified by changing the immersing condition.

2. Experimental

The solution used for the microporous silica coating is syn-

thesized from a mixture of tetramethoxysilane ($\text{Si}(\text{OCH}_3)_4$, Kanto >98%), water, hydroxyacetone ($\text{CH}_3\text{COCH}_2\text{OH}$, Kanto >80%) as the catalyst, and methanol (Wako >99.5%) as the solvent. The molar ratio of $\text{Si}(\text{OCH}_3)_4:\text{H}_2\text{O}:\text{CH}_3\text{COCH}_2\text{OH}$ is 1:1:5. Water is deionized by an AQUARIUS GS-200 System (Advantec), while the other reagents are used without further purification. The mixture is stirred at 25°C for 24 hours and then aged at 40°C for four days. 2-Ethoxyethanol (Wako >98%) is added to the solution, and methanol is removed by evaporation in order to smooth the surface of the coating film. The coating solution is dropped onto a PET (SANPLATEC), nonluminescent quartz plate (Tosoh) or mirror polished silicon wafer (Komatsu Electronics >99.9999%) and spun at 1000 rpm for 60 s at 25°C. The coating on the substrate is dried at 25°C or 80°C for two hours, immersed in water at 80°C for two hours and then dried at 25°C.

The pore structure of the coating is determined by the nitrogen gas adsorption/desorption technique (Micromeritics ASAP2020) for the bulk gel prepared from identical silicate precursors. The thickness of the coatings is measured using a surface profilometer (ULVAC Dektak 6M). The pencil hardness of the coating on a silicon wafer is measured by a Japanese Industrial Standard method (JIS-K-5400). The optical transmission spectra of the coating on a quartz glass are obtained using an UV-visible spectrometer (Shimadzu UV-2100) in the wavelength range of 300–800 nm. The surface morphology of the coating on a silicon wafer was observed using an atomic force microscope (AFM, Seiko Instruments SPA400). The surface wettability of the coating on a silicon wafer was evaluated from the contact angle measurement at room temperature using a contact angle meter (Kyowa Interface Science DropMaster 300). The averaged contact angle was calculated from five measured values at different points of the coating. The Fourier transform infrared (FT-IR) spectra of the coating were measured with an FT-IR spectrometer (Shimadzu IRPrestige-21), which was attached to an attenuated total reflection (ATR) unit equipped with a monolithic diamond prism crystal, in the range of 700–4000 cm^{-1} .

3. Results

The superhydrophilicity was developed by coating a PET substrate with microporous silica and immersing the microporous silica coating in water at 80°C as compared to hydrophobicity of a bare PET substrate. **Figure 1** shows that a water droplet spread out on the superhydrophilic silica-coated PET, while a semispherical droplet of water remained on the hydrophobic bare PET.

The superhydrophilic coating of silica was highly transparent as shown in the inset of **Fig. 2**. Transparent quartz was used as a substrate instead of the PET since the surface of the PET substrate is rough. **Figure 2** shows the optical transmission spectra of the coating on a transparent substrate of quartz in the wavelength range of 300–800 nm. The transmittance of the silica coating reached approximately 100% of incidence in the visible region.

The superhydrophilic coating was smooth in the presence of micropores. **Figure 3** (a) shows an AFM topographical image of the coating on a highly smooth silicon substrate. A smooth silicon substrate was used instead of the PET substrate since the surface of the PET substrate is rough. A typical cross-sectional profile (**Fig. 3**(b)) indicates a vertical interval within 3 nm. The roughness was only three percent of the thickness of the coating (100 nm). The roughness due to a

Fig. 1. A superhydrophilic coating on a PET substrate on the left half and a hydrophobic bare PET substrate on the right half. After coating half of the substrate with microporous silica, the coatings are immersed in water at 80°C for two hours that causes hydrolysis of the remaining alkoxy groups. Water is sprayed after drying the half-coated substrate at 25°C for one day.

Fig. 2. Optical transmission spectra of a superhydrophilic coating on a quartz substrate. The inset is a photograph of the superhydrophilic coatings on a quartz substrate.

micropore in the coating is visually imperceptible.

The specific surface areas of dried bulk gel, which was prepared from coating sol, are shown in **Table 1**. Immersing silica in water at 80°C increased the specific surface area of the silica (700 $\text{m}^2 \text{g}^{-1}$) compared to that of the as-prepared one (410 $\text{m}^2 \text{g}^{-1}$). The increase in the specific surface area was caused by the pore distribution change. **Figure 4** shows the nitrogen adsorption-desorption isotherms for the as-prepared silica and two kinds of silica immersed in water. The isotherm is I type for all of the silica, which indicates that the high specific surface area of the silica is due to the microporous structure.⁶⁾ The pore size for the as-prepared silica has a narrow distribution and a mode diameter of the pore is less than 0.8 nm.

Fig. 3. (a) An AFM topographical image of a superhydrophilic coating on a silicon substrate. (b) A typical cross-sectional profile. The thickness of the coatings is estimated to be 100 ± 2 nm.

Table 1. Immersion Effects on the Silica Coating

Immersing temperature	Film thickness / nm	Specific surface area / m^2g^{-1}	Pencil hardness	Contact angle
80 °C	100	700	2H	3.4°
25 °C	100	510	2H	11.6°
as-prepared	105	410	2B	29.5°

Immersing a microporous silica in water at 80°C expanded the mode diameter of the pore to 0.8 nm.

Hydrolysis of the remaining alkoxy groups proceeded by immersing the silica coating in water at 80°C. **Figures 5 and 6** show the infrared spectra of the as-prepared coating and two kinds of coatings immersed in water at 25°C and 80°C. Immersing the silica coating in water increased the absorptions at a broad band centered near 3400 cm^{-1} , a small band at 1630 cm^{-1} and a sharp band at 950 cm^{-1} (Fig. 5). The broad band centered near 3400 cm^{-1} is assigned to the hydrogen bonded SiO-H stretching vibrations ($3200\text{--}3650\text{ cm}^{-1}$), hydrogen bonded water ($3300\text{--}3500\text{ cm}^{-1}$) and hydrogen bonded OH vibrations of alcohols ($3300\text{--}3600\text{ cm}^{-1}$) which are possibly of methanol, 2-ethoxyethanol and hydroxyacetone in the case of this study.^{(6)–(8)} The small band at 1630 cm^{-1} is assigned to the scissor bending vibration of the adsorbed molecular water, while the band at 950 cm^{-1} is assigned to the Si-OH stretching of the terminal silanol groups.^{(7)–(9)} An isolated SiO-H stretching vibrations, which occurs at $3650\text{--}3800\text{ cm}^{-1}$,⁽⁷⁾ is not detected in these spectra. This result indicates that most of the silanol groups in these silica coatings are hydrogen bonded to water. The distinguishing band of hydroxyacetone, which is

Fig. 4. Nitrogen adsorption (open)/desorption (solid) isotherms of the silica powders (a) immersed in water at 80°C for two hours, (b) immersed in water at 25°C for two hours, and (c) as-prepared.

Fig. 5. FT-IR spectra at $700\text{--}4000\text{ cm}^{-1}$ of the silica coatings on a silicon substrate (a) immersed in water at 80°C for two hours, (b) immersed in water at 25°C for two hours, and (c) as-prepared.

observed at 1715 cm^{-1} , was not detected in all of the spectra. On the other hand, immersing the silica coating in water decreased the absorptions bands at 2950 and 2850 cm^{-1} (Fig. 6). These bands are assigned to the C-H stretching of the alkoxy groups.^{(10),(11)} The alkoxy groups remained in the as-prepared coating. The reaction system for the preparation of the microporous silica involved only a molecule of water per tetramethoxysilane molecule to leave the alkoxy groups after hydrolysis and condensation. The hydroxyl group increased whereas the alkoxy group decreased. Hydrolysis of

Fig. 6. FT-IR spectra at 2800–3000 cm^{-1} of the silica coatings on a silicon substrate (a) immersed in water at 80°C for two hours, (b) immersed in water at 25°C for two hours, and (c) as-prepared.

Fig. 7. Thermo-gravimetry of the silicas (a) immersed in water at 80°C for two hours, (b) immersed in water at 25°C for two hours, and (c) as-prepared.

the remaining alkoxy groups to hydroxyl groups proceeded by immersing the silica coating in water. Absorption bands, which consist of a shoulder at 1220 cm^{-1} and distinct peak at 1080 cm^{-1} , are slightly increased by immersing the silica coating in water. These bands are assigned to the longitudinal optical (LO) mode and the transverse optical (TO) mode of the asymmetric Si-O stretching vibration, respectively,^{7),8)} whereas the band at 800 cm^{-1} , the intensity of which almost did not change when immersing in the water, is assigned to the symmetric Si-O-Si stretching or vibrational modes of the ring structure.^{12),13)} The change in the Si-O bonds is not recognizable due to the small rate of change in the initial quantity.

Immersing microporous silica in water at 80°C facilitated the adsorption of water on the micropores of the silica. Based on the thermogravimetry, for the silica immersed in water at 80°C, the mass decrease developed in two stages (Fig. 7 (a)): rapid elimination of the adsorbed water below 120°C and gradual elimination of hydroxyl groups through dehydrating condensation over a wide range of temperatures. The amount of adsorbed water on the silica immersed in water at 80°C is almost four times greater than that on the as-prepared silica. The hydrolysis of the remaining methoxy groups to hydroxy groups facilitated the adsorption of water on the micropores of the silica. The behavior of the mass decrease of the silica immersed in water at 25°C was similar to that at 80°C (Fig. 7 (b)). The amount of water adsorbed on the silica immersed in water at 25°C is lower than that at 80°C, which depended on a decrease in the surface area or the pore volume. Methoxy groups slightly remained after immersing the silica in water at 25°C, while they were completely removed during the immersion at 80°C. The elimination process of the as-prepared silica was more complicated (Fig. 7 (c)). Organic functional groups, such as methoxy groups, and high boiling point organic compounds, such as hydroxyacetone and 2-ethoxyethanol, remained in the as-prepared silica. The mass decreases were observed to occur in two steps: the decrease at 120–200°C was attributed to the combustion of hydroxyacetone and 2-ethoxyethanol and the decrease at 200–300°C was

Fig. 8. Water drops onto the silica coatings on a silicon substrate (a) immersed in water at 80°C for two hours, (b) immersed in water at 25°C for two hours, and (c) as-prepared. (d) Semispherical drop of water on a bare silicon substrate.

attributed to the combustion of the methoxy groups.

Immersing a silica coating in water increased the hardness of the coating. The pencil hardness of the coating immersed in water was 2H, while that of the as-prepared coating was 2B (Table 1). By immersing the silica coating in water, a silica network will develop by hydrolysis of the remaining alkoxy groups and subsequent condensation of the generated hydroxy groups. The hardnesses of the coatings were quite different between the as-prepared silica coating and the coating immersed in water, although the thicknesses of all the coatings were about 100 nm.

The superhydrophilicity was developed by immersion in water at 80°C. The water contact angles, which were observed with a silica coating on a silicon substrate, are shown in Table 1. A drop of water immediately spreads over the coating immersed in water at 80°C (Fig. 8 (a)), on which contact

angle was 3°. The contact angle on the coating immersed in water at 25°C was 10° (Fig. 8 (b)), while the contact angle on the as-prepared coating was 29° (Fig. 8 (c)). The hydrophilicity depended on the extent of the hydrolysis of the methoxy groups. In contrast, the contact angle on a bare silicon substrate was 70° (Fig. 8 (d)).

4. Discussion

The superhydrophilic silica coating was prepared below 80°C and thereby applied to the coating on a polymer substrate such as a PET (Fig. 1). The micropores of the silica coatings are filled with water due to the adsorption of water. The presence of the infrared absorption band attributed to the hydrogen bonded O-H vibrations and the mass decrease attributed to water elimination suggested water adsorption on the surface OH groups. The water drop is in contact with a rough surface which consists of the solid and the adsorbed water with which the micropore is filled.

The contact angle of water on the coating immersed in water at 25°C, which has the remaining methoxy group, was 10°. The presence of the infrared absorption band attributed to the C-H vibrations suggested residual methoxy groups. The remaining methoxy group would decrease the adsorption of water. The TG data suggested that the amount of water adsorbed on the silica immersed in water at 25°C is lower than that at 80°C.

Hydroxyacetone as a non-ionic catalyst allows the preparation of the microporous silica precursor from tetramethoxysilane under neutral condition. As before, the microporous silica precursor has been hardly obtained and then the porosity is controlled by slowing the rate of evaporation as compared to the rate of condensation. In fact, the microporous bulk gel is readily obtained by the slow drying.^{6),14)} On the other hand, we controlled the porosity by accelerating the rate of the catalytic hydrolysis with hydroxyacetone.

The pore size distribution was narrow and most of the pores are smaller than 1.5 nm in diameter. The pore size was so small that an apparently smooth surface was obtained.

Immersing the silica coating in water is an important process for removing not only the methoxy group, but also hydroxyacetone as a non-ionic catalyst. Accessibility to the back of the coating depended on the immersion temperature. The hardness of the coating immersed in water at 25°C is the same as that at 80°C. Therefore, hydrolysis of the methoxy groups and the subsequent condensation of the hydroxyl groups would have already occurred at the surface layer of the coating. An increase in hardness of the silica coating immersed in water was also reported by Matsuda et al.¹⁵⁾

5. Conclusion

A transparent smooth superhydrophilic microporous silica

coating on a PET substrate was developed by the hydrolysis of the remaining methoxy groups to hydroxy groups and the adsorption of water on the inner surface of the micropores at 80°C. After the drying of the adsorbed water, the superhydrophilicity can be restored by the adsorption of water at a normal humidity and room temperature.

A microporous silica coating can be prepared from the microporous precursor sol, which was prepared from the simple silicon alkoxide under neutral conditions by accelerating the rate of the condensation with hydroxyacetone. Immersing the coating in water is an important process for removing not only the methoxy group, but also the hydroxyacetone.

Acknowledgements This work was supported by the Nagano Knowledge Cluster Initiative from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References

- 1) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, **388**, 431–432 (1997).
- 2) J. Bico, U. Thiele and D. Quéré, *Colloids Surf. A*, **206**, 41–46 (2002).
- 3) F. Ç. Cebesi, Z. Wu, L. Zhai, R. E. Cohen and M. F. Rubner, *Langmuir*, **22**, 2856–2862 (2006).
- 4) K.-C. Song, J.-K. Park, H.-U. Kang and S.-H. Kim, *J. Sol-Gel Sci. Tech.*, **27**, 53–59 (2003).
- 5) Y. Murakami, K. Tanaka, Y. Takechi, S. Takahashi, Y. Nakano, T. Matsumoto, W. Sugimoto and Y. Takasu, *J. Sol-Gel Sci. Tech.*, **29**, 19–24 (2004).
- 6) C. J. Brinker and G. W. Scherer, "Sol-Gel Science," Academic Press, New York (1990) pp. 818–823.
- 7) P. Innocenzi, *J. Non-Cryst Solids*, **316**, 309–319 (2003).
- 8) A. Zecchina, S. Bordiga, G. Spoto, L. Marchese, G. Petrini, G. Leofanti and M. Padovan, *J. Phys. Chem.*, **96**, 4991–4997 (1992).
- 9) R. M. Almeida and C. G. Pantano, *J. Appl. Phys.*, **68**, 4225–4232 (1990).
- 10) D. L. Ou and A. B. Seddon, *J. Non-Cryst. Solids*, **210**, 187–203 (1997).
- 11) J. Méndez-Vivar and A. Mendoza-Bandala, *J. Non-Cryst. Solids*, **261**, 127–136 (2000).
- 12) C. J. Brinker and G. W. Scherer, "Sol-Gel Science," Academic Press, New York (1990) pp. 541–546.
- 13) M. Nocuñ and M. Handke, *J. Mol. Struct.*, **596**, 139–143 (2001).
- 14) G. C. Frye, A. J. Ricco, S. J. Martin and C. J. Brinker, "Better Ceramics Through Chemistry III," Ed. by C. J. Brinker, D. E. Clark and D. R. Ulrich, Mat. Res. Soc., Pittsburgh, Pa. (1988) pp. 349–354.
- 15) A. Matsuda, T. Matoda, T. Kogure, K. Tadanaga, T. Minami and M. Tatsumisago, *J. Sol-Gel Sci. Tech.*, **27**, 61–69 (2003).