Control of the oxidizing and hydrophilicizing properties of photocatalytic TiO₂ thin films coated on a polyethylene-terephthalate substrate

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Polyethylene-terephthalate (PET) films coated with photocatalytic TiO₂ and silicone as a binder were fabricated and attached to a window pane. A white substance was observed on the surface after exposure for several months in an area with air pollution. The white substance was analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy, ion chromatography and capillary electrophoresis, and was identified as CaSO₄. Although the oxidizing properties of the films were affected by the particle size and the amount of TiO₂ in the photocatalytic layer, the hydrophilicizing properties of the films were hardly changed by them. In this study, we found that it was possible to decrease the oxidizing properties of photocatalytic PET films while maintaining the hydrophilicizing properties constant by using small TiO₂ particles and controlling the ratio of TiO₂/binder.

Key-words: Titanium dioxide, Photocatalyst, Particle size, Oxidizing property, Hydrophilicizing property

1. Introduction

When a photocatalytic titanium dioxide thin film is continuously irradiated with ultraviolet (UV) rays, the water contact angle of the film surface gradually decreases until it reaches 0 degrees.¹ This state is called “super-hydrophilicity”. In this state, the photocatalytic thin film is not clouded by steam or dew since water cannot become droplets on the film and thus we obtain an antifogging effect. Rain droplets enter spaces between the dirt and the photocatalytic thin film because the film surface is more susceptible to water than dirt. The dirt is then washed away with rain and we obtain a self-cleaning effect.² This photocatalytic hydrophilicity has potential for a wide number of applications. As a result of our research, the hydrophilicizing properties in the absence of UV rays were largely improved by combining TiO₂ with SiO₂.³ The possibility for photocatalyst application is now stronger.

Binding crystalline TiO₂ and SiO₂ particles to the substrate usually requires calcination at a very high temperature. This limits the substrate material considerably. However, a polyorganosiloxane with the composition of the same SiO₂ showed adhesion to the substrate by forming a three-dimensional network structure at low temperature. The use of polyorganosiloxane as a bonding material to fix photocatalytic TiO₂ particles to the substrate makes a transparent thin film with super-hydrophilicity possible.

There have been a number of preparations of TiO₂–SiO₂ composites or glasses described,⁴–⁶ as well as studies of photocatalysts produced by TiO₂ and SiO₂ particles.⁷–⁹ For example, Iketani et al.⁰ reported the photocatalytic activities of highly transparent TiO₂/Poly-dimethylsiloxane hybrid films prepared on Polymethyl methacrylate (PMMA) substrates by a sol–gel method. Takami et al.¹⁰ prepared a SiO₂/TiO₂/PMMA thin film by single coating from the combination of tetraethyl orthosilicate (TEOS) and titanium tetraisopropoxide (TTIP), and examined the performance of the film as a low reflective coating. However, no study on the practical application of a TiO₂/SiO₂ system’s film, containing problems of real use for self-cleaning window glass and the improvement of the problem, has been reported.

Since the outside of window glass becomes dirty so easily, the cleaning of window glass in a multistoried building is usually done by not a machine but directly a person. Cleaning at great heights is dangerous, and so it is desirable that the cleaning frequency be as little as possible. Applying photocatalytic polyethylene-terephthalate (PET) film to a window glass will provide a self-cleaning effect, which will make it possible to reduce the cleaning frequency. When a PET film that formed the transparent photocatalytic thin layer of a TiO₂/silicone was exposed for several months, a white substance was observed on the surface of the film. Because this white film ruined the visibility and appearance of the transparent glass body, its generation needed to be controlled in real use. The object of the present study was to examine the formation mechanism of the white substance and to find the conditions necessary to prevent the generation of the substance, while maintaining its hydrophilicizing properties. The relationship between the TiO₂ particle size, as well as the ratio of TiO₂/silicone and its oxidizing and hydrophilicizing properties, was investigated. The white substance was observed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS). The ions adhered on the exposed film were analyzed by ion chromatography and capillary electrophoresis. The oxidizing properties of the films were measured by the decomposition rate of methylmercaptan (CH₃SH) gas and methylene blue solution. The hydrophilicizing properties were evaluated from the contact angle of water under UV irradiation.

2. Experimental procedures

2.1 Preparation of film samples

Methylic alcohol (CH₃OH; 223.5 parts by weight) and ethyl silicate 40 (Colcoat Co. Ltd. Tokyo, Japan; oligomer of ethyl
silicate) (30 parts by weight) were placed in a 500 mL beaker, and stirred uniformly at 303 K. Nitric acid (HNO₃; 60% by weight) was diluted with distilled water (45 parts by weight) and added to the above solution. The temperature was maintained at 303 K while the solution was hydrolyzed for 6 h. The hydrolyzed solution of silicone obtained was referred to as solution A. The solid SiO₂ content of solution A was 4 wt%.

Solution A (25 parts by weight) and isopropyl alcohol (70 parts by weight) were placed in a 200 mL beaker, and stirred uniformly at 303 K for about 1 h. Anatase TiO₂ sol STS-01 (Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) (5 parts by weight), shown in Fig. 1(a), was added to the above solution. The mixture of TiO₂ and silicone obtained here was referred to as solution B. The solid SiO₂ content of solution B was 2.5 wt%.

Solution B was coated on a PET substrate film with a PE resin anchor layer by using a Meyer bar 2, and heated to hardening for 3 min at 393 K. A protection layer with a thickness of 0.5 μm was formed (Fig. 2). Solutions with different TiO₂/silicone ratios, such as 80/20, 60/40, and 30/70 wt%, were prepared.

Silicone resin paints KP-85 (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan; solid content 20%) were coated on a 38 μm-thick PET substrate film with a 4 μm anchor layer (PE resin) of 20 × 20 cm size by using a Meyer bar #2, and heated to hardening for 3 min at 393 K. A protection layer with a thickness of 3 μm was formed in this treatment. Titanium (TiO₂) sol/silicone mixtures such as solution B were coated onto this protection layer by using a Meyer bar #1 and were heated until hardening for 3 min at 393 K. A TiO₂/silicone surface layer with a thickness of 0.5 μm was formed (Fig. 2).

### Table 1: Specifications of TiO₂ sols

| TiO₂ sol | (a) STS-01 | (b) GHN-6 | (c) STS-100 |
|----------|------------|-----------|-------------|
| SEM image | ![SEM image](image1) | ![SEM image](image2) | ![SEM image](image3) |
| Crystal type | Anatase | Anatase | Anatase |
| Mean particle size (DLS) | 49 nm | 40 nm | 32 nm |
| Crystallite size (XRD) | 7.71 nm | 6.41 nm | 4.97 nm |
| Solid content | 30 wt% | 20 wt% | 20 wt% |
| pH | 1.5 | 1.5 | 1.2 |

Fig. 1. Specification and SEM photographs of TiO₂ sol.

Fig. 2. Schematic illustration of photocatalytic PET film.

2.2 Exposure test on the outside of the window-glass

The conventional PET film and the photocatalytic PET film samples were attached to the outside of window glass and exposed for about 2 months at the following locations.

(I) Toranomon/Minato-ku, Tokyo Met. [Air pollution: large, Surrounding environment: near an intersection where traffic is very heavy.]

(II) Chigasaki-shi/Kanagawa Pref. [Air pollution: moderate, Surrounding environment: along a road where traffic is heavy, and near the seashore.]

(III) Gotemba-shi/Shizuoka Pref. [Air pollution: small, Surrounding environment: the foot of a mountain where traffic is very light.]

After outdoor exposure tests, the presence of dirt and white substance on the surface of the film was observed and measured. Figure 3 shows the outline of the evaluation. The adhered substance on the surface of the glass or PET films after outdoor exposure for about 2 months in the above-described location (I) was moved to the adhesive layer (Fig. 2).
tapes. Whole adhesive tapes were deposited onto platinum. The shape was observed and analyzed quantitatively by using a field emission-type scanning electron microscope (FE-SEM; Model S-4100, Hitachi Ltd., Tokyo, Japan) equipped with an energy-dispersive X-ray (EDS; Model EMAX2700, Horiba Ltd., Kyoto, Japan) analysis system. The ions on the surface of the glass and PET films was collected by using quartz wool with distilled water and removed as an insoluble substance from the water by using a filter with a pore diameter of 0.2 mm. The solution, including various dissolved ions, was measured by using a capillary electrophoretic apparatus (Model HP319CE, Hewlett-Packard Japan, Ltd., Tokyo) and an ion chromatograph apparatus (Model IC-7000, Yokogawa Analytical Systems Inc., Tokyo, Japan).

2.3 Characterization

Before preparing the mixture of TiO2 sol and silicone, such as solution B, the mean particle diameters of anatase TiO2 sols, such as those shown in Fig. 1, were measured by using a dynamic light scattering particle size distribution analyzer (Model DLS-600, Otsuka electronics Co., Ltd., Osaka, Japan). These sols were milled by agate mortar after drying at 333 K in an air bath in order to make the powder. The mean crystallite size of the powder was measured by the Scherrer method with an X-ray diffractometer (Model MXP-18, Mac Science, Kanagawa, Japan).

The decomposition rates of CH3SH gas in the PET film samples, as well as the decomposition rate of methylene blue and the contact angle of water, were measured when irradiated with UV rays. The measurement of the CH3SH gas decomposition rate during UV irradiation was performed as follows. A film sample with an area of 100 cm2 was placed in the center of a 6 L glass container. Methylmercaptan (CH3SH) gas was injected into the container so that the initial concentration was 1 mW/cm2. The solution, including various dissolved ions, was measured by using a capillary electrophoretic apparatus (Model MXP-18, Mac Science, Kanagawa, Japan).

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The composition of the PET film was measured by using a contact angle meter (Model CA-X150, Kyowa Interface Science Co., Ltd., Saitama, Japan) by dropping water from a microcylinder to the surface after 30 s, while irradiating the surface of the film with UV rays for 24 h with a 20-W BLB fluorescent light until the UV intensity reached 1 mW/cm2.

3. Results and discussion

3.1 Identification and reaction process of the white substance on the photocatalytic PET film

In the exposure studied at (I) Toranomon/Tokyo and (II) Chigasaki-shi/Kanagawa, a white substance was generated on the surface of a photocatalytic PET film containing large TiO2 particles and a low binder ratio (Fig. 4), it did not appear on the surface of the window glass and conventional PET film. In the exposure at (III) Gotemba-shi/Shizuoka, no white substance was generated. As for the formation of the white substance, the exposure results suggest that both degree of air contamination and photocatalytic activities of the surface layer are related.

Figure 5 shows the measurement results of ion concentrations on the surface of the window glass, conventional PET film, and photocatalytic PET film. As shown in Fig. 5, the ion amount existed in the conventional PET film did not differ from that on the surface of the window glass. On the other hand, a larger amount of NH4+, Ca2+, NO3-, SO42- and a smaller amount of Cl-, HCO3- were detected on the surface of the photocatalytic

![Fig. 4. Pictures of photocatalytic PET film; (a) before, and (b) after exposure for 2 months at Tokyo.](image)

![Fig. 5. Ion concentrations of the surface of window glass, conventional PET film, and photocatalytic PET film after 2 months at Toranomon/Tokyo as analyzed by capillary electrophoresis and ion chromatograph.](image)
PET film with respect to those detected on the window glass. Figure 6 shows the SEM photographs and EDS spectra of adhered substances on the glass and films. As shown in the SEM photographs of Fig. 6(c), pillar-shaped crystals were observed on the surface of the adhesive tape where the white substances were gathered. As shown in the EDS spectra of Fig. 6(c), large peaks of Ca and S were detected from these pillar-shaped crystals. These results suggest that the white substance was a mixture of salt with $\text{NH}_4^+$, $\text{Ca}^{2+}$, $\text{NO}_3^-$, and $\text{SO}_4^{2-}$. In addition, since the crystal is pillar shaped and insoluble in rainwater, it was estimated to be calcium sulfate (CaSO$_4$).

The mean concentrations of nitrogen oxide (NO$_x$) and sulfur oxide (SO$_x$) gas from April 1998 to March 1999 at (I) Chiyoda-ku/Tokyo, (II) Chigasaki-shi/Kanagawa, and (III) Gotemba-shi/Shizuoka are shown in Fig. 7(a). The mean ion concentrations contained in the rainwater from April 1998 to March 1999 throughout the neighborhood and the surrounding environment in the above-described (I)–(III) locations are shown in Fig. 7(b).

Since we carried out the outdoor exposure tests of this research from 1998 to 1999, the public data of same period was selected and referred in Fig. 7. There was no public data of the same place (which see section 2.2) carried out the exposure test, so we selected and referred the neighborhood location as Figs. 7(a) and 7(b) Chiyoda-ku/Tokyo, and 7(b) Hiratsuka-shi/Kanagawa. As shown in Fig. 7(a), there were sufficient amounts of NO$_x$ and SO$_x$ gas in (I) Chiyoda-ku/Tokyo and (II) Chigasaki-shi/Kanagawa.
As shown in Fig. 7(b), several ions such as $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Na}^+$ and $\text{Ca}^{2+}$ were supplied by rainwater. It is characteristic of rainwater in an urban region such as Chiyoda-ku/Tokyo to contain a large amount of $\text{SO}_4^{2-}$ and $\text{NH}_4^+$. It is also characteristic of rainwater in a seashore region such as Hiranaka-shi/Kanagawa to contain a large amount of $\text{Cl}^-$ and $\text{Na}^+$.

The following reaction processes, (3)–(6), can be offered for the data of SEM-EDS, Fig. 7, and the photocatalytic oxidation of TiO$_2$.

\[
\text{TiO}_2 \xrightarrow{\text{h}^+} \text{h}^+ + \text{e}^- \quad (3)
\]

\[
\text{NO}_2^-(\text{NO}_2^-, \text{NO}_3^-) \xrightarrow{\text{OH}} \text{NO}_3^- \xrightarrow{\text{O}_2} \text{H}_2\text{O}_3 \quad (4)
\]

\[
\text{SO}_4(\text{SO}_2) \xrightarrow{\text{OH}} \text{SO}_2^{2-} \xrightarrow{\text{H}^+} \text{H}_2\text{SO}_4 \quad (5)
\]

\[
\text{SO}_2^{2-} \xrightarrow{\text{Ca}^{2+}} \text{CaSO}_4(s) \downarrow \quad (6)
\]

\[
\text{Cl}^- \xrightarrow{\text{H}^+} \text{HCl(g)} \uparrow \quad (7)
\]

\[
\text{CO}_3^{2-} \xrightarrow{\text{H}^+} \text{CO}_2(g) \uparrow + \text{H}_2\text{O} \quad (8)
\]

As shown in reaction process (3), photocatalytic TiO$_2$ generates a positive hole-electron pair when it is irradiated with UV rays. Active oxygen such as hydroxy radical (·OH) and super oxide ion (O$_2^-$) are then made by combining $\text{OH}^-$ and O$_2$ in air, respectively. It is important to note that active oxygen has a very strong oxidizing power. Both experimental locations in (I) Toranomon/Tokyo and in (II) Chigasaki-shi/Kanagawa are regions where there is a lot of traffic, and thus many NO, SO$_2$, and Cl$_2$ are present in the atmosphere due to the exhaust gas of automobiles. These NO$_2$, SO$_2$, and Cl$_2$ are oxidized by ·OH and become HNO$_3$, HSO$_3$, and HCl, respectively. The explanation for the presence of a considerable amount of $\text{NH}_4^+$ and $\text{Ca}^{2+}$ in the photocatalytic PET film (which see Fig. 5) as compared with rainwater is as follows. The acidity of the surface had risen by generating HNO$_3$ and $\text{H}_2\text{SO}_4$ as shown in reaction processes (4) and (5), respectively. In order to neutralize these acid, basic gaseous matter in the atmosphere such as ammonia and Ca aerosol was absorbed. The explanation for the small amounts of Cl$^-$ and HCO$_3^-$ in the photocatalytic PET film (which see Fig. 5) as compared with rainwater is that HCl and CO$_2$ were generated and volatilized as shown in reaction processes (7) and (8), respectively.

### 3.2 Hydrophilicizing and oxidizing properties at various TiO$_2$ particle sizes and TiO$_2$/binder ratios

Figure 8 shows the measurement results of the water contact angle to UV irradiation time when the TiO$_2$ particle size and the ratio of TiO$_2$/binder were varied. The contact angle of water with the films composed of TiO$_2$/silicone at ratios of 80/20–60/40 wt% did not depend on the TiO$_2$ particle size, which decreased to $<10^\circ$ within 3 h of UV irradiation, and hardly changed afterward. When examined in detail, the contact angle after UV irradiation of films that used small-sized (~32 nm) TiO$_2$ particles was a few degrees higher than that of films that used large (~49 nm) and also moderately-sized (~40 nm) TiO$_2$ particles. On the other hand, in the film containing a TiO$_2$/silicone ratio of 30/70 wt%, the contact angle of water rose immediately after preparation, and did not decrease readily even if the film was irradiated with UV rays. No films with a TiO$_2$/silicone ratio of 30/70 wt% became super-hydrophilic because the contact angle with water did not fall below 20°, even if they were irradiated with UV rays for 120 h.

Figure 9 shows SEM photographs of the surface of the photocatalytic layer on the PET films. The surface microstructures were heavily dependent on the amount of silicone binder in the photocatalytic layer. In the film containing a TiO$_2$/silicone ratio of 30/70 wt%, as shown in Figs. 9(a)(III), 9(b)(III), and 9(c)(III), TiO$_2$ particle was distributed on substrate side and hardly exposed on the surface side because of thick silicone layer. These results suggest that, in the composition range of TiO$_2$/silicone of 80/20–60/40 wt%, it is possible to prepare a super-hydrophilic film that has a $\sim$5° contact angle with water by UV irradiation, regardless of the TiO$_2$ particle size selected.

Figure 10(a) shows the measurement results of the CH$_3$SH gas decomposition rate and Fig. 10(b) shows the measurement results of the methylene blue decomposition rate, when UV rays irradiated photocatalytic PET films in which the TiO$_2$ particle size and TiO$_2$/binder ratio were varied. The decomposition rate of CH$_3$SH gas became the index of the oxidizing power to the atmospheric gas. Similarly, the decomposition rate of methylene blue became the index of the oxidizing power to substances.
carried by rainwater that adhered to the surface of the photocatalytic PET films. As shown in Fig. 10, photocatalytic films with larger TiO₂ particles and larger TiO₂/binder ratios showed a tendency towards higher oxidizing power. Photocatalytic films with TiO₂/silicone = 80/20 wt% had little oxidizing power, independent of the TiO₂ particle size. The reason is that there was few amount of TiO₂ that was able to be exposed on the surface of the film as shown in Figs. 9(a)(III), 9(b)(III), and 9(c)(III). These results suggest that the oxidizing power can be controlled by varying the TiO₂ particle size or the TiO₂/binder ratio in the range of TiO₂/silicone = 80/20–60/40 wt%.

3.3 Optimum condition of TiO₂ particle size and TiO₂/binder ratio

As shown in Fig. 4(b) in section 3.1, because the white substance was generated after exposure, large TiO₂ particle (~49 nm) and a low binder ratio such as TiO₂/silicone = 80/20 wt% was not suitable composition. As well as the ratio of TiO₂/silicone = 30/70 wt% was not suitable, because it can hardly control the oxidizing power and hydrophilicizing property, even if the TiO₂ particle size is changed. We inferred that TiO₂/silicone = 60/40 wt% was the optimum composition of the photocatalytic layer, because it could balance good hydrophilizing properties with suitable oxidizing power.

To confirm the optimum composition that we can control both the hydrophilicizing property and oxidizing power without white substance generation, photocatalytic PET film samples that contained a varied TiO₂ particle size with TiO₂/silicone = 60/40 wt% were made again. In order to compare with exposure test in section 3.1, control sample with large-sized (~49 nm) TiO₂ particle was added. They were attached on the window glass and exposed at the Toranomon/Tokyo location. After 2 months of exposure, the exposed surface of all the samples showed the super-hydrophilicity (contact angle of water < ~5°). The film sample with small-sized (~32 nm) TiO₂ particle, the white substance was not observed. However, the white substance was observed on the film surface that used large (~49 nm) and moderately-sized (~40 nm) TiO₂ particles.

Figure 11 shows the result of the ion concentrations on the surface of the photocatalytic PET films after exposure for about 2 month. In the film that used small-sized (~32 nm) TiO₂ particle, the oxidizing power was suppressed, and especially the amounts of SO₄²⁻ as oxidizing forms of SO₂ were decreased. Because the amount of Ca²⁺ collected also decreased, it was estimated that the generation of CaSO₄ decreased as well.

4. Conclusions

In this research, PET films coated with thin TiO₂/silicone were
prepared. The white substance generated during exposure was identified by using SEM-EDS, capillary electrophoresis, and ion chromatographs. Its hydrophilicizing and oxidizing properties varied with TiO₂ particle size and TiO₂/silicone ratio. The results were as follows:

(1) The white substance generated on the photocatalytic film was identified as insoluble CaSO₄. The SO₄²⁻ oxidized from the SOₓ in the atmosphere by a photocatalyst reacted with Ca²⁺ brought from rainwater or aerosol to form CaSO₄.

(2) In the range of TiO₂/silicone = 80/20–60/40 wt %, the film surface showed super-hydrophilicity (contact angle of water under ~5°) after UV irradiation independent of the TiO₂ particle size.

(3) The oxidizing power of the photocatalytic film increased with an increase in the ratio of TiO₂/silicone, and TiO₂ particle size increase.

(4) The oxidizing power of the photocatalytic film can be controlled while maintaining the hydrophilicity constant by selecting a reasonable TiO₂ particle size and/or TiO₂/binder ratio.

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