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An Organic–Inorganic Hybrid Composite as a Coating Agent

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Abstract An organic–inorganic hybrid composite for use as a coating agent was prepared by mixing linseed oil with hydrophobic octylsilyl titanium dioxide particles having an average diameter of 35 nm (OSI-TIO2-35) in volatile silicone. The weight ratio of linseed oil with OSI-TIO2-35 was varied from 2:8 to 8:2 and the mixture was spread on a glass plate by dragging an applicator across it. After storing in the oven at 60 °C for 2 days, the composite having the weight ratio of OSI-TIO2-35 with linseed oil at 8:2 exhibited very high water-repellent properties having a water contact angle of 148°. Variation of the water contact angle during storage at 60 °C was monitored. It decreased by 10° in the initial 8 h and then increased by 45° over the next 2 days. Composites containing silicone resin, TMSS BY11-018, instead of linseed oil were also prepared. The sample having a weight ratio of OSI-TIO2-35 with TMSS BY11-018 at 8:2 also exhibited very high water-repellent properties with a water contact angle of 152°. The highly hydrophobic surface thus prepared by the coating and drying of those organic-inorganic hybrid composites was easily transferred to highly hydrophilic surfaces by calcination at 500 °C for 3 h.

Keywords Coating · Water-repellent · Highly hydrophobic · Highly hydrophilic · Linseed oil · Hydrophobic octylsilyl titanium dioxide particle · Silicone resin · Drying · Calcination

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Introduction

A highly hydrophobic surface possessing highy water-repellent properties is desirable for self-cleaning, anti-fouling, and anti-contamination coatings. Recently, many new technologies for preparing highly hydrophobic surfaces have been developed [1–6]. The new technologies are categorized into two groups, i.e. development of new highly hydrophobic materials and procedures to fabricate micro- or nano-structures on the hydrophobic surface. After the finding of super-water-repellent properties of fractal surfaces of the alkylketene dimer by Onda et al. [7], more efforts have been devoted to the later approach. In the former approach, chemical modification by introducing fluorine is the most general procedure, since it lowers the surface free energy [8]. The water-repellent properties of fluorinated compounds, however, are not very high. The water contact angle on the surface of regular aligned closely hexagonal packed—CF_3 was reported to be around 120° [9]. After the publication of this report, attempts to fabricate micro- or nano-structures on poly(tetrafluoroethylene) (PTFE), the most familiar non-sticking polymers [10], started [11].

Most of the methods to fabricate micro- or nano-structures on a hydrophobic surface thus developed, however, are unlikely to be available for mass production of water-repellent surfaces in the factory because of the high cost of processing and the difficulty in magnifying the scale of production. In addition, strong endurance of the micro- or nano-structures was required for the permanence of the water-repellent property. Thus, the development of a new highly hydrophobic material has actually been expected from a real industrial point of view. Here, we have developed an organic-inorganic hybrid composite, a mixture of hydrophobic octylsilyl titanium dioxide particles having an average diameter of 35 nm (OSI-TIO2-35) and linseed oil or silicone resin, as a highly hydrophobic coating agent. Linseed oil has been traditionally used as a raw material of paint, ink and coating agents, since it is dried by autoxidation in the presence of atmospheric oxygen [12, 13]. A coating agent containing linseed oil and a nano-particle filler has also been developed [14]. A highly hydrophobic coating agent using linseed oil and nanoparticles, however, has not been developed.

Recently, unfavorable influences by some kinds of fluorinated chemicals such as perfluorooctanoic acid (PFOA) on humans and animals have been reported [15, 16]. Reports of the influence of PFOA on humans and animals are now widespread not only in the United States but also throughout the whole world [17, 18]. The highly hydrophobic coating agent developed in this study does not contain any fluorinated chemicals.

Not only highly water-repellent surfaces but also highly hydrophilic surfaces are desirable for self-cleaning, antifouling, and anti-contamination coatings. Water droplets find it hard to stick to the former surface, while the water rapidly spreads on the latter surface to form a very thin liquid film that evaporates easily. Recently, the superhydrophilic property of the photocatalysis of titanium dioxide has attracted much attention [19–21]. UV light irradiation of titanium dioxide led to an increase in the number of hydroxyl groups on the surface, and this makes the surface highly hydrophilic [22]. However, photocatalysis of titanium dioxide possesses a highly hydrophilic property only in the presence of UV irradiation. The water contact angle gradually increases within minutes to hours after stopping the irradiation. In contrast, the highly hydrophilic properties of sol–gel derived SiO_2–TiO_2 composite films persists [23, 24]. In these cases, the highly hydrophilic property is not due to the photocatalysis of titanium dioxide, but has been attributed to an enhanced acidity at the SiO_2–TiO_2 interfaces. Although the sol-gel methods are extensively utilized in industrial manufacturing, there are still some problems, such as, aggregation of titanium dioxide [25], hyporeactivity of the reagents [26], the transformation into the oxide from the hydroxide [27], cracks in the coatings [28], and phase separation [29]. In this study, the water-repellent surface prepared by using the composite was shown to be easily transformed into a highly hydrophilic surface by calcination.

Experimental Procedures

Materials

Highly hydrophobic particles, OSI-TIO2-35, were prepared by following the patented method for the preparation of dispersible particle for cosmetics [30]. Titanium dioxide particles having an average diameter of 35 nm coated with silica and alumina (TIO2-35) supplied by Tayca Corporation were octylsilyl-modified to make the surface hydrophobic. To a mixture of 1,000 g of TIO2-35 and 3,000 g of 2-propanol, 100 g of octyltriethoxysilane purchased from Dow Corning Toray Co., Ltd. was added and the suspension was dispersed in a bead mill. All volatile compounds in the resulting suspension were removed by evaporation at 70 °C to obtain OSI-TIO2-35. Transmission electron microscope (JEM-230, JEOL Ltd.) images of TIO2-35 and OSI-TIO2-35 are shown in Fig. 1. No large differences in size were observed in TIO2-35 and OSI-TIO2-35, indicating that octylsilylation did not change the size of the particle.

An organic-inorganic hybrid composite for producing a coating agent was prepared by mixing OSI-TIO2-35 with linseed oil (PV = 7.4 mequiv/kg and AV = 1.2 mg KOH/g) in decamethylcyclopentasiloxane (DMCPSI), a volatile silicone, purchased from Shin-Etsu Chemical Co., Ltd. by supersonic agitation. The weight ratio of OSI-TIO2-35 with linseed oil was varied from 2:8 to 8:2 and the weight of DMCPSI was 1.15 times the sum of the weight of OSI-TIO2-35 and linseed oil. OSI-TIO2-35 was also mixed with silicone resin, trimethylsiloxysilicate BY11-018 (TMSS BY11-018), purchased from Dow Corning Toray

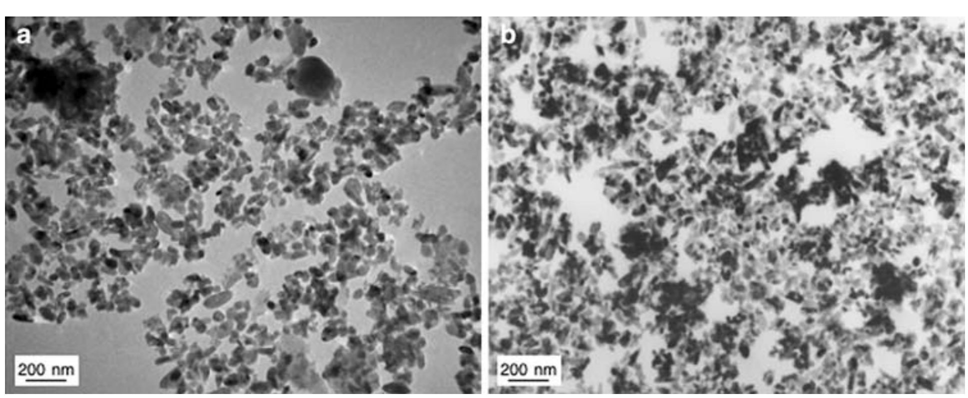


Fig. 1 TEM images of **a** TIO2-35 and **b** OSI-TIO2-35

Co., Ltd. in DMCPSI, and its property as a coating agent was evaluated.

Coating and Drying and Calcination

The suspension of OSI-TIO2-35 and linseed oil in DMCPSI thus prepared was coated on a glass plate using a linear motor coater assembled from a linear motor actuator (LMS-30-C2-L555-5.0, PBA Systems. Pte Ltd.) and an applicator (SA-201, Tester Sangyo Co, Ltd.). The suspension was dropped beside the applicator onto the glass plate and spread by moving the stage at a constant velocity. The gap of the applicator was set at 0.5 minch (=12.7 μm) and the velocity of the moving plate was 5.0×10^{-3} m s^{-1}. The coated glass plate was dried in an oven at 60 °C. The suspension of OSI-TIO2-35 and TMSS BY11-018 in DMCPSI was also coated onto a glass plate by the same procedure.

There are two successive processes of drying, i.e. evaporation of the volatile DMCPSI followed by drying of the linseed oil by autoxidation. The former was completed within 1 h and virtually no evaporation of the linseed oil was detected. In the case of using TMSS BY11-018, only the evaporation of the volatile DMCPSI is the drying process. Some samples after 1 h drying in the oven at 60 °C were calcined in a furnace at 500 °C for 3 h.

Water Contact Angle

The contact angle of a 2.0-μL water droplet on the surface was measured using a contact angle meter (DropMaster 500, Kyowa Interface Science Co., Ltd.). The water contact angle was calculated from the CCD camera image of the water droplet by integrated multi-functional analysis software (FAMAS, Kyowa Interface Science Co., Ltd.).

Results and Discussion

Hydrophobic Property of Surface

Before the analysis of the hydrophobicity of the surfaces of the coated sample, a suspension of OSI-TIO2-35 in DMCPSI was coated onto a glass plate and the water contact angle on the surface was evaluated after the completion of the evaporation of DMCPSI. Though some parts of particles were removed from the glass surface and adsorbed onto the water droplet surface during the measurement, the water contact angle was determined to be 149°. The surface was thus highly hydrophobic, but was not lasting. Exposing the sample plate to water removed most of the OSI-TIO2-35 particles from the glass plate. The particle thus should be mixed with other materials to prepare the coating agent.

In the case of using linseed oil for the preparation of the samples, hydrophobicity of the surface was influenced by the content of the hydrophobic OSI-TIO2-35 as shown in Fig. 2a. The water contact angle was not changed by increasing the weight ratio of OSI-TIO2-35 with linseed oil from 2:8 to 6:4 but increased with increasing the ratio from 6:4 to 8:2. Hydrophobicity of the surface was also influenced by the drying of linseed oil by autoxidation. The water contact angle of every sample increased by 20–40° after storing in the oven at 60 °C for 1 day, while a small enhancement of hydrophpobicity was observed after one more day of drying. In order to check the influence of the drying of linseed oil on the hydrophobicity, the evolution of the water contact angle over time for the surfaces coated by the composite having the weight ratio of OSI-TIO2-35 with linseed oil at 76:24 was monitored. As shown in Fig. 3, the water contact angle decreased by 10° in the initial 8 h then increased by 50° over the next 2 days. No apparent change in the water contact angle was observed with 3 more days of storing in the oven at 60 °C. A solidified linseed oil surface prepared on a glass plate by drying in the oven at 60 °C exhibited a water contact angle of 85° and further storing in the oven did not change the hydrophobicity as shown in Fig. 3.

The surface coated by the linseed oil–OSI-TIO2-35 composite having the weight ratio of OSI-TIO2-35 with linseed oil at 8:2 exhibited a water contact angle of 148° after drying in the oven at 60 °C for 2 days. The water-repellent property is thus almost the same as the one of the surface on which only OSI-TIO2-35 was coated. The enhancement of the hydrophobicity by the drying of

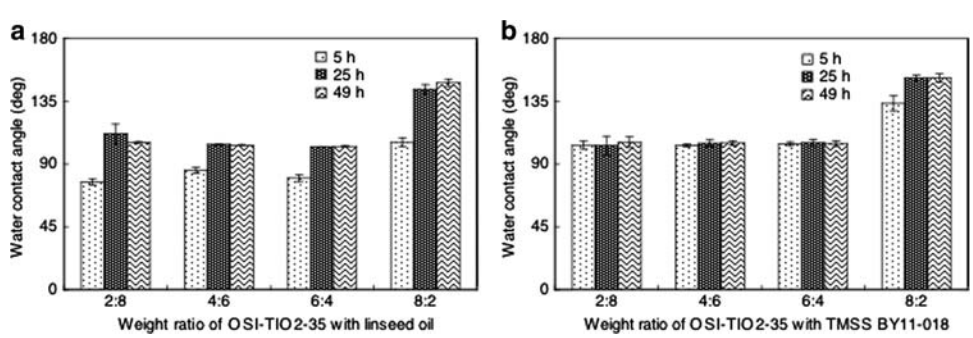


Fig. 2 The water contact angle on a surface coated with **a** a linseed oil–OSI-TIO2-35 composite and **b** a TMSS BY11-018–OSI-TIO2-35 composite. The values after storing in the oven at 60 °C for 5, 25, and 49 h are shown

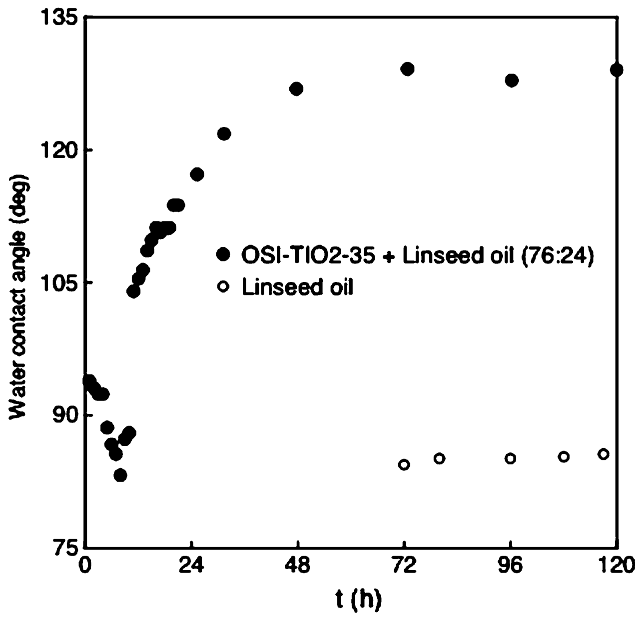


Fig. 3 The evolution of water contact angle over time on a surface coated with the linseed oil–OSI-TIO2-35 composite and linseed oil during storing at 60 °C for 5 days. A composite sample having the weight ratio of OSI-TIO2-35 with linseed oil at 76:24 was used

linseed oil allowed the water-repellent property of the composite to increase to the level of highly hydrophobic OSI-TIO2-35. Since the sample surface was solidified by the drying of linseed oil, no removal of material from glass surface was observed by exposing the sample plate to water. The highly water-repellent surface is thus durable unlike the surface on which only OSI-TIO2-35 is coated. In addition, the organic–inorganic hybrid composite developed in this study is fluorine-free.

As shown in Fig. 2, hydrophobicity of the composites consisting of linseed oil and TMSS BY11-018 were almost identical after storing in the oven at 60 °C for 1 and 2 days. Highly water-repellent surface with a water contact angle of 151° was realized by preparing the composite having a weight ratio of OSI-TIO2-35 with TMSS BY11-018 of 8:2. Since it was solidified by the evaporation of DMCPSI, the highly water-repellent surface was also durable and the material was also fluorine-free. The enhancement of the water contact angle by storing in the oven, however, was small for the composites consisting of TMSS BY11-018.

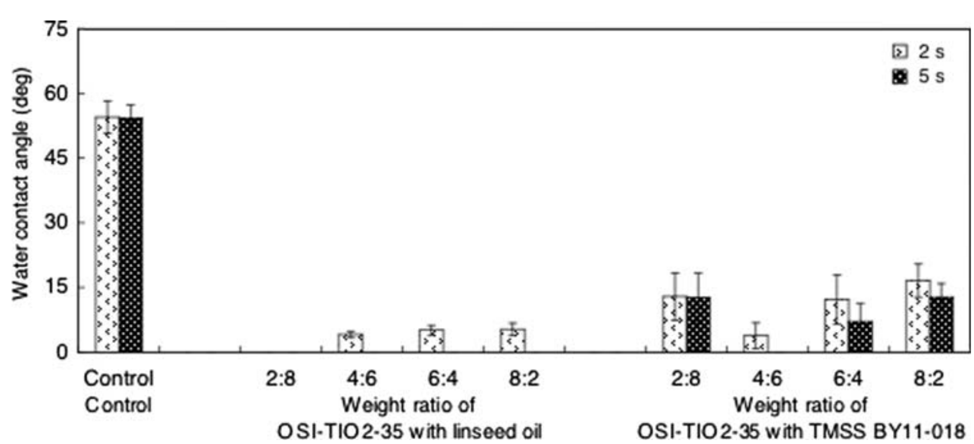
Calcination

Calcination as well as drying by autoxidation and evaporation of volatile material are extensively used for solidifying coating agents on surfaces. In this study, not only drying of linseed oil and evaporation of volatile silicone but also calcination were employed to make the surface solid. The property of the surface after 3 h of calcination in the furnace at 500 °C was very different from the one obtained by 1 or 2 days of storing in the oven at 60 °C. As shown in Fig. 4, all surfaces were hydrophilic and their water contact angle was far less than the one of control calcined glass plate. Especially, the calcined linseed oil–OSI-TIO2-35 composites were strongly hydrophilic. Less than 5 s were required to realize 0° of water contact angle on all calcined linseed oil–OSI-TIO2-35 composites.

The temperature of 500 °C was high enough to burn out the linseed oil. In addition, both TMSS BY11-018 and octylsilyl groups on the surface of the OSI-TIO2-35 particle were transformed to silica by the calcination. All the hydrophobic groups thus disappeared and the surface was transformed to a SiO_2–TiO_2 composite film that was reported to exhibit highly hydrophilic properties [23, 24].

The organic-inorganic hybrid composites developed in this study are suitable for both highly hydrophobic and highly hydrophilic coatings. In addition, the composites are fluorine free. They may be applied as self-cleaning, anti-fouling, and anti-contamination coatings.

Fig. 4 The water contact angle on surfaces coated with a linseed oil–OSI-TIO2-35 composite and a TMSS BY11-018–OSI-TIO2-35 composite after being calcined at 500 °C for 3 h. The values 2 and 5 s after attaching a 2.0-μL water droplet on the sample surface are shown



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