Preparation of Highly Water-repellent Surface by Spontaneous Formation of Double Scale Roughness Pattern

Pascal Joly, Akihiro Kuroda and Kouichi Asakura*
Faculty of Science and Technology, Keio University (3-14-1 Hiyoshi, Kohoku, Yokohama 223-8522, JAPAN)

Abstract: Hydrophobic organic-inorganic hybrid composite suspensions were prepared by mixing hydrophobic octylsilyl titanium dioxide particles having average diameter of 35 nm with drying oil or moisture cure room temperature vulcanization silicone gum in volatile silicone. They were spread on a glass plate by using a linear motor coater and an applicator. Spatially periodic stripe patterns parallel to the direction of dragging the applicator were usually generated. The phenomenon is called directional viscous fingering, i.e. spontaneous pattern formation by the growth of fluctuation in morphology of mobile interface during the dragging coat. The pattern spontaneously formed on the surface became double scale when stored samples were coated. In this case, the large scale spatially periodic pattern was formed by the directional viscous fingering and the small ragged random pattern may be due to the giant molecules formed by cross-linking of silicone gum. Double scale roughness patterns were also generated by double dragging coat. The large and small scale pattern was formed by the first and second dragging coat, respectively. The formation of double scale roughness enhanced the water-repellent property of the hydrophobic surface. In some cases, water contact angle increased by 20° to realize super water-repellent surface with a value exceeding 150°.

Key words: water-repellent, double scale roughness, directional viscous fingering, dragging coat, dissipative structure

1 INTRODUCTION

Surfaces with high water-repellent properties have attracted a great deal of attention lately due to their large range of application. Treatment of surface of satellite antennas to reduce snow adhesion\(^1\), hydrophobic clothes\(^2\), biomedical coating to prevent protein adsorptions\(^3\) are a few examples of possible applications. Water-repellent properties can be characterized by their water contact angle, the measurable angle that a water droplet makes with a solid. The water contact angle is influenced by two parameters, surface free energy and surface roughness. It, however, is 120° even for the lowest free energy surface based on \(-\text{CF}_3\) alignment\(^4\). Thus, surface roughness must be adjusted for fabricating super water-repellent surface having water contact angle more than 150°. In fact, some plants are famous for their high water-repellent properties, such as the lotus leaves due to a double scale roughness. This phenomenon was named the lotus effect\(^5\). Based on a regular spaced pillar model, Patankar showed how double scale roughness structures could lead to water-repellent\(^6\). Also, the influence of double scale roughness pattern dimension using pillar like structures was studied by Bushan and Jung\(^7\). Various methods to mimic the lotus effect have been achieved until now, mostly by fabricating rough structures on the top of hydrophobic surfaces\(^8\). However, most of the methods developed are expensive and therefore inadequate for mass production.

Here, we investigated the influence of mesoscopic and microscopic double scale roughness structure on water-repellent property. We focused on stripe patterns that appear during a coating process due to the phenomenon called directional viscous fingering\(^9\), which is an example of dissipative structure, i.e. self-organization in far-from-equilibrium system\(^10,11\). Viscous fingering is a fingering pattern formation through a growth of morphological fluctuation in the mobile interface of two immiscible fluids. The directional viscous fingering is a particular case of viscous fingering that happens when a
thin film of viscous fluid is produced by passing it through a small gap. It is also generated when two pieces of adhesive tapes that are stuck together are peeled. In our previous study, the generation of directional viscous fingering pattern of organic–inorganic hybrid composite suspension during its dragging coat on a glass plate was studied. Formation of spatially periodic single scale stripe patterns by the directional viscous fingering alone, however, did not change the water–repellent property of the surface. Additional microscopic dewetting patterns did not change the water–repellent property of the surface. In this study, attempts were made to fabricate double scale roughness for water–repellent surface only by the dragging coat. The composite used was a mixture of volatile silicone, hydrophobic octylsililataion of titanium dioxide particles having average diameter of 35 nm, and drying oil or moisture cure room temperature vulcanization silicone gum whose properties have been investigated in our previous study.

2 EXPERIMENTAL

2.1 Materials

A volatile silicone, decamethyl cyclopentasiloxane (DMCPSI), was purchased from Shin–Etsu Chemical Co., Ltd. Moisture cure room temperature vulcanization silicone gum SE 738 (Si–RTV) was purchased from Dow Corning Toray Co., Ltd. Commercially available linseed oil having peroxide value of 7.4 meq·kg⁻¹ and acid value of 1.2 mgKOH·g⁻¹ was used. A hydrophobic particle having an oil adsorption of 40 m²·g⁻¹, OSI–TIO2–35, that was produced by the octylsililataion of titanium dioxide particle was supplied from TAYCA Corp. Organic–inorganic hybrid composite suspension for coating agent was prepared just before the coating by mixing the suspension of OSI–TIO2–35 in DMCPSI with linseed oil (sample: A) or Si–RTV (sample: B). But, in some cases, the composites containing Si–RTV were stored for 7 days at 25°C in a place in which relative humidity was at 50% (sample: B*). During this storage Si–RTV was partially solidified. The weight ratio of the composite suspension was OSI–TIO2–35 : linseed oil or Si–RTV : DMCPSI = 32 : 10 : 82 in all experiments.

2.2 Methods

2.2.1 Coating and Drying

The composite suspension was coated on a glass plate by following the method employed in our previous report. The sample A, B, or B* was dropped beside the applicator on the glass plate placed on the linear motor coater and spread by moving the stage at constant velocity. Dragging coat was realized by setting the scale of the applicator gap at 0.5 minch (=12.7μm). The coated glass plate was dried in the oven at 60°C. In some cases, the second dragging was performed on the sample surface stored in the 60°C oven for 24 h. For the second dragging, no gap was set on the applicator.

2.2.2 Analysis of Surface Structure

Surface structure of the samples realized was analyzed using surface profile measuring system Dektak 3030 (Sloan Technology Corporation). Only average thickness of the composite was measured when the surface was flat, while heights and positions of five tops and bottoms were measured when the patterns were generated. In order to characterize the surface structure, heights of the top and bottom of the stripe pattern, h_t and h_b, were calculated by averaging heights of the five tops and bottoms, and the characteristic length of a spatial periodicity, λ, was calculated by averaging the distance between adjacent five tops and bottoms. In order to characterize the spatial periodicity, wave number, q=(2π/λ), was also calculated.

2.2.3 Characterization of Water–repellent property

Water–repellent properties can be characterized by the contact angle of 2.0 μL of water droplet on the surface. The contact angle was measured by contact angle meter (DropMaster 500, Kyowa Interface Science Co., Ltd.) and calculated from the CCD camera image of water droplet by integrated multi–functional analysis software (FAMAS, Kyowa Interface Science Co., Ltd.).

3 RESULTS AND DISCUSSION

3.1 Spatial pattern spontaneously formed by dragging coat

In our previous study, the composite suspension consists of octyl p–methoxycinnamate, OSI–TIO2–35, and DMCPSI. It was found to form spatially periodic stripe pattern when it was spread by the applicator on a glass plate at constant velocity. The spontaneous pattern formation was due to the phenomenon called directional viscous fingering. A critical point on the dragging velocity for the fingering instability, v_c, was clearly observed. The same behavior was also observed when the sample A or B containing linseed oil or Si–RTV instead of octyl p–methoxycinnamate was spread. Velocity of the moving plate was chosen between 1.0 × 10⁻² m·s⁻¹ and 7.0 × 10⁻¹ m·s⁻¹. An example chart of the surface profile measurement is shown in Fig. 1 (a). Stripe pattern that formed parallel to the dragging direction was spatially periodic. Two types of bifurcation diagrams, dragging velocity – wave number plot and dragging velocity – peak height plot, were obtained as shown in Fig. 2 (a) and (b). Non–zero value of wave number q and double plots for the height h_t and h_b for single dragging velocity are the indication of stripe pattern formation. In both cases,
dragging velocity is the parameter that constrains the system far-from-equilibrium, and the bifurcation point was clearly observed. The value of \( v_c \) for the sample \( B \) was smaller than the one for the sample \( A \). The sample \( B \) tended to form larger wave number pattern than the sample \( A \). The height of tops and bottoms of the stripe pattern of both surfaces were almost identical.

Not only freshly prepared samples but also the composite suspensions containing Si–RTV stored for 7 days at 25°C in a place in which relative humidity was at 50% (sample \( B^* \)) was spread by the same procedure. Si–RTV is a moisture cure room temperature vulcanization silicone gum that reacts with water to form cross-linking structure. Giant molecules were thus formed by the cross-linking in the presence of atmospheric moisture to increase the viscosity of the sample during the seven days of storage. When the dragging velocity was equal to or less than \( 5.0 \times 10^{-4} \) m·s\(^{-1}\), the pattern was not single scale but double scale as shown in the example chart of Fig. 1 (b).

The large scale spatially periodic pattern was formed by the directional viscous fingering and the small ragged random pattern may be due to the giant molecules formed by cross-linking of Si–RTV. The double scale roughness was fabricated by this extremely simple procedure. In
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In these cases, the values for $h_T$ and $h_B$ were not clearly determined, while the value of $q$ could be approximately determined. Thus, only a dragging velocity – wave number plot was obtained as a bifurcation diagram as shown in Fig. 2 (c). The characteristic length of the stripe pattern shown in Fig. 1 (b) can be estimated to be around 0.5 mm that is almost 2/3 of the value calculated from the chart of Fig. 1 (a). Spreading condition and the initial composition of the samples B and B$^*$ are the same. Characteristic length of the directional viscous fingering decreases with increasing viscosity$^{9,14}$. The smaller characteristic length obtained by using sample B$^*$ is thus due to its higher viscosity. The patterns became random when the dragging velocity was at $7.0 \times 10^{-1}$ m·s$^{-1}$. In these cases, no clear distinction between two scales of patterns was determined.

The other procedure to fabricate double scale roughness is double dragging. The sample A or B was initially spread on a glass plate then the plate was dried in the 60°C oven for 24 h. In addition to the evaporation of DMCPSI that was mostly completed by 1 h of drying, solidification of linseed oil or Si–RTV proceeded during this process to increase the viscosity of the surface. The second dragging setting the gap of the applicator at 0 µm was performed on these surfaces. The surface was thus scraped under the weight of the applicator. Figure 3 shows an example of surface profile before and after the second dragging. Small ragged structure was formed on the top of the large spatially periodic initial directional viscous fingering pattern. This is due to the directional viscous fingering of highly viscous surface. In addition, small projections were formed at each bottom part of the initial stripe patterns. This may be due to the pressure applied from the applicator. The double scale roughness was again fabricated by the extremely simple procedure.

3.2 Water-repellent property of the patterned surface

In our previous report, hydrophobicity of the composite containing linseed oil was found to change during the
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drying process at 60°C and be constant after 48 h of drying\textsuperscript{16}). The measurement of the water contact angle was done after 24, 48, and 60 h of drying in the 60°C oven. It was independent of time for drying when sample B and B* were spread, while it increased by about 20° when time for drying was increased from 24 h to 48 h for sample A. Figure 4 shows the water contact angle of the surface prepared by single dragging coat and 48 h of drying. The surface coated by sample B and dried exhibited higher water-repellent property than the one coated by sample A and dried. This difference is due the intrinsic difference of hydrophobicity between dried linseed oil and cross-linked Si–RTV. In both cases, the water contact angle was independent of dragging velocity. Spatially periodic stripe pattern by the directional viscous fingering was generated when the dragging velocity was equal to or more than 3.0 × 10\textsuperscript{-1} m·s\textsuperscript{-1} and 1.0 × 10\textsuperscript{-1} m·s\textsuperscript{-1} for sample A and B, respectively. The patterned surface, however, did not exhibit higher water contact angle than the flat surface, indicating that the generation of single scale stripe pattern having characteristic length of 0.4–1.4 mm and the height level distance from top to bottom of 2–4 µm does not enhance the water-repellent property. On the other hand, the water contact angle on the surface coated by sample B* and dried was around 10° higher than the one on the surface coated by sample B and dried. Fabrications of double scale roughness on the surfaces by this very simple method are thus useful for preparing highly water-repellent surface exhibiting the water contact angle more than 150°.

Double scale roughness was also fabricated by the double dragging coat. Figure 5 shows the contact angle of water on the surface prepared by double dragging coat. In both cases, water-repellent property was enhanced by the second dragging. Enhancement of the contact angle of water was around 20° for sample A and 10° for sample B.

Fig. 4 Water Contact Angle on the Surfaces on which the Samples A, B, and B* Were Coated and Dried for 48 h at 60°C.

Preparation of highly water-repellent property exhibiting contact angle of water more than 150° was again realized by this very simple method.

5 CONCLUSION
More than 30 years have passed since Ilya Prigogine was awarded the 1977 Nobel Prize in Chemistry for his establishment of the concept called dissipative structure, i.e. self-organization in far-from-equilibrium systems due to the growth of fluctuations\textsuperscript{10,11}). After that, many theoretical and experimental works on the pattern formation in far–from–equilibrium systems have been performed in the field of basic physics, chemistry, and biology. Industrial technology based on the concept of dissipative structure, however, has scarcely been developed. Out–of–equilibrium conditions are ubiquitously generated in manufacturing processes such as coating. The pattern formation in far–from–equilibrium condition during coating process, however, is usually considered as the phenomenon that should be avoided.

In the present study, double scale roughness structured surfaces were fabricated by very simple procedures, i.e. just coating the stored samples or the double dragging coat, by utilizing far–from–equilibrium pattern formation due to the growth of fluctuations. Highly water-repellent surfaces exhibiting the water contact angle more than 150° were prepared. Unlike our previous report\textsuperscript{14}), no water shower processes to generate dewetting patterns are required for enhancing the water contact angle. In addition, magnification of the scale production by this
method is easily possible. This kind of new technologies based on the concept of dissipative structure may lead to a true revolution in many manufacturing processes, since the concept itself is quite new in this field.

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References