Super Water-Repellent Surfaces Resulting from Fractal Structure

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Super water-repellent surfaces showing a contact angle of 174° for water droplets have been made of alkylketene dimer (AKD). Water droplets roll around without attachment on the super water-repellent surfaces when tilted slightly. The AKD is a kind of wax and forms spontaneously a fractal structure in its surfaces by solidification from the melt. The fractal surfaces of AKD repel a water droplet completely and show a contact angle larger than 170° without any fluorination treatments. Theoretical prediction of the wettability of the fractal surfaces has been given in the previous paper.[3] The relationship between the contact angle of the flat surface θ and that of the fractal surface θ_f is expressed by the equation $\cos\theta_f = (L/l)^{D-2}\cos\theta$ where $(L/l)^{D-2}$ is the surface area magnification factor. The fractal dimension of the solid AKD surface was determined to be $D \approx 2.3$ applying the box-counting method to the SEM images of the AKD cross section. L and l, which are the largest and the smallest size limits of the fractal behavior of the surface, are also estimated from the box-counting method. The contact angles of some water/1,4-dioxane mixtures on the fractal and the flat AKD surfaces were determined, and the values of $\cos\theta_f$ were plotted against $\cos\theta$. The plot of $\cos\theta_f$ against $\cos\theta$ agrees well with the theoretical prediction. It has been demonstrated by this work that the fractal concept is a powerful tool to develop some novel functional materials.

1. Introduction

Wettability of solid surfaces with a liquid (water in particular) is a very important phenomenon in our daily life as well as in many industrial processes. The wettability is governed by two factors. One is the chemical factor, and the other is the geometrical (surface structural) factor of the solid surfaces.[1,2] Water-repellent surfaces are usually designed by the former factor utilizing the low surface free energy of fluorinated compounds. We have paid special attention to the geometrical structure of solid surfaces and found the excellent effectiveness of fractal structure on the wettability.[3] In our previous paper, we have provided the theoretical results on the wettability of fractal surfaces and the experimental verification of the theoretical prediction.[3] The present paper is an extension of the previous work, and deals with the experimental realization of super water-repellent surfaces that repel completely the water droplet.

The contact angle θ between a flat solid surface and a liquid droplet is given by Young's equation (1).

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \qquad (1)$$

where γ_{SL}, γ_S, and γ_L denote the interfacial tensions of the solid−liquid, the solid−gas, and the liquid−gas interfaces, respectively. Wenzel suggested that the contact angle θ' of a liquid droplet placed on the rough solid surface was written as eq 2.

$$\cos\theta' = \frac{r(\gamma_S - \gamma_{SL})}{\gamma_L} \qquad (2)$$

where r is a roughness factor, which is defined as the ratio of actual surface area of a rough surface to the geometric projected area. Then, the relationship between θ' and θ is given by eq 3.

$$\cos\theta' = r\cos\theta \qquad (3)$$

Equation 3 indicates that the rough surface will be more water-repellent (more wattable) to a liquid when θ is greater (less) than 90°. In this work, fractal structure is adopted as an extremely rough surface to achieve the super water-repellent surfaces.

2. Experimental Section

2.1. Materials. Alkylketene dimer (AKD) was synthesized by the procedures shown in Figure 1.[4] Precautions were taken to dry glassware and organic solvents to avoid hydrolysis of AKD to dialkylketone (DAK). Stearoyl chloride (60.6 g) (Tokyo Chemical Industry Co., Ltd.) dissolved in 100 mL of toluene was added dropwise to a solution of triethylamine (22.3 g) (Tokyo Chemical Industry Co., Ltd.) in 300 mL of toluene at 323 K with stirring in a glass flask. After the reaction finished, the by-product of triethylamine hydrochloride was filtered off at 323 K. Crude AKD sample was obtained with a weak brown color by evaporating the solvent in vacuo. The crude AKD was purified by using a silica-gel column under the following conditions: 35 g of the crude AKD in 200 mL of a chloroform/n-hexane mixture (6/4 in volume) was put on a silica-gel (C200; WAKO) column gently and eluted with the chloroform/n-hexane mixtures having gradients of 0/100 to 50/1. Pure AKD (mp = 66−67 °C) was obtained as the early fractions of the elute. The brown-colored impurities in the crude AKD were readily adsorbed on the top of the silica-gel column. The impurities of fatty acid, DAK, and oligomers in the crude AKD are also separated out by this purification procedure using a silica-gel column. Special care is necessary not to exceed 5 min in the column chromatography, otherwise the decomposition of AKD will start to occur probably because of the catalytic action of the silica-gel. The final sample of the AKD was

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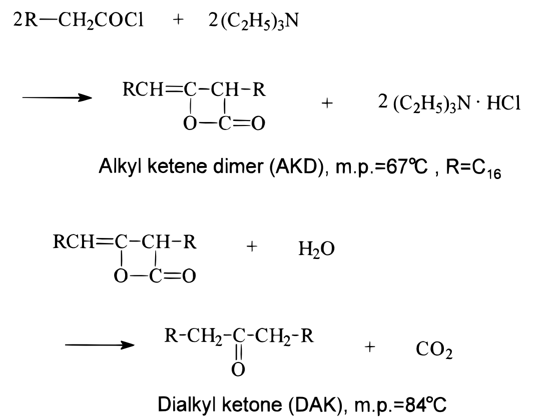

Figure 1. Synthetic procedures of alkylketene dimer (AKD) and dialkyl ketone (DAK).

checked to be more than 98% pure by gas chromatography (GC), GPC, and titration technique of the β-lactone ring. A main impurity still remaining was the DAK. GPC analysis was done with a column of TSK gel-2000H (Tosoh Co., Ltd.) and a RI detector, using THF as an eluting solvent. The monomethylamine (MMA) titration method was utilized to determine the concentration of β-lactone ring of the AKD molecule.

Repeated recrystallization of the crude AKD from *n*-hexane was not effective enough to remove the DAK. The AKD sample purified by the recrystallization method, however, showed super water-repellency, even if it contained 5−10 wt % DAK. This result suggests that the DAK does not impede formation of a super water-repellent surface with AKD. The DAK was sometimes used as an additive to control the fractal dimension of AKD surfaces. The DAK (mp = 84 °C) was obtained as a third fraction in the silica-gel chromatography mentioned previously. 1,4-Dioxane was purchased from Kanto Chemical Co. and used without further purification. Water used in the contact angle measurements was deionized and once distilled.

2.2. Preparation of Super Water-Repellent AKD Surfaces. Super water-repellent surfaces were prepared by solidification from the melted mixtures of AKD and DAK. The mixing ratio of AKD/DAK was changed from 10/0 to 8/2 to obtain the different fractal dimensions of the surfaces. A AKD (precontaining ∼2 wt % DAK)/DAK mixture was put on a glass plate (76 mm × 26 mm × 1 mm) and heated at 363 K on an electric hot plate. After the mixture melted, the glass plate was cooled down to room temperature in a dry nitrogen gas atmosphere, and the AKD sample was allowed to solidify. The microscopic observations under a crossed polarizer of this solidification process show that the DAK with a higher melting point forms first some crystalline nuclei and the AKD crystals grow from these nuclei. The higher mixing ratio of DAK results in the formation of a greater number of nuclei. This may be the reason why the fractal dimension of the AKD surface can be controlled by the DAK content. The water-repellency of the AKD surface progressively improves for about 3 days and finally shows the super water-repellency having a contact angle larger than 170°.

2.3. SEM Observations of the AKD Cross Section. To estimate the fractal dimension of the AKD cross section, a AKD film peeled off from a glass plate was cleaved with the aid of a razor blade, and the AKD film so obtained was set to the aluminum sample stage using an electroconductive paste (Fujikura-kasei Co., Ltd., Type D-550). After Pt−Ag evaporation onto the sample surface, the field emission scanning electron microscope (FE-SEM; Hitachi, S-4000) images of its cross section were taken at several magnifications (×150, ×1500,

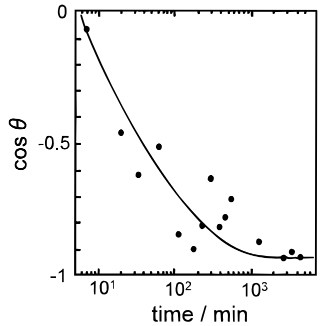

Figure 2. Contact angles of water droplets of ∼1 mm diameter on a solid AKD surface plotted against curing time of the AKD crystal after solidification of the melted AKD. Equilibrated contact angle was obtained after about 3 days. Solid AKD was left standing for curing in a dry N_2 gas atmosphere. Each datum point is an averaged value of 3−5 water droplets placed on different positions of one AKD surface. The AKD sample surfaces prepared independently and taken out of the drybox at appropriate intervals were used for one run of the contact angle measurement.

×6000, and ×30000) to estimate the scale of self-similarity of the AKD surface.

2.4. Contact Angle Measurements. Wettability of the AKD surfaces was evaluated by the contact angle measurements with an optical contact angle meter (Kyowa Interface Science Co. Ltd., type CA-A). Aqueous solutions of 1,4-dioxane were used as the sample liquids. The surface tension of the liquid changes from 36 mN/m for pure 1,4-dioxane to 72 mN/m for pure water, depending upon the concentration of 1,4-dioxane. A liquid droplet of about 1mm diameter was dropped carefully onto an AKD solid surface from a height of 5 cm and then given gentle vibration by tapping the sample stand with a finger to obtain the equilibrium contact angle.

3. Results

3.1. Super Water-Repellency of AKD Surfaces. The contact angles of water on an AKD surface are plotted against time elapsed after AKD solidification in Figure 2. The contact angle of a water droplet placed on the AKD surface increases with time after solidification and finally becomes greater than 170° after 3 days (Figure 3a). SEM observations indicate that the AKD surface just after solidification has no special structure in the surface. After 3 days, however, the solid surface exhibits extreme roughness with some stratified structures, as shown in Figure 4. One can see from the figure that there are two kinds of structures of roughness. One has a spherical shape having a scale of roughness of about 30 μm, and the other is a flakelike structure, the scale of which is about 1 μm. This stratified structure suggests that the AKD surface is fractal as actually substantiated later. The water-repellency and the surface structure of roughness can be controlled by the ratio of AKD and DAK mixed. The size of the spherical structure mentioned above becomes smaller, and the number of structures increases with increasing concentration of DAK.

The AKD sample with a flat surface is also prepared as a reference by mechanical cutting with a knife. The surface is confirmed to be flat by SEM observations. The flat surface is, of course, not very water-repellent, showing a contact angle not larger than 109° (Figure 3b). One can understand consequently that the super water-repellency of the surface can be realized by the surface roughness of the AKD.

3.2. Determination of the Fractal Dimension of Super Water-Repellent AKD Surfaces. The box-counting method

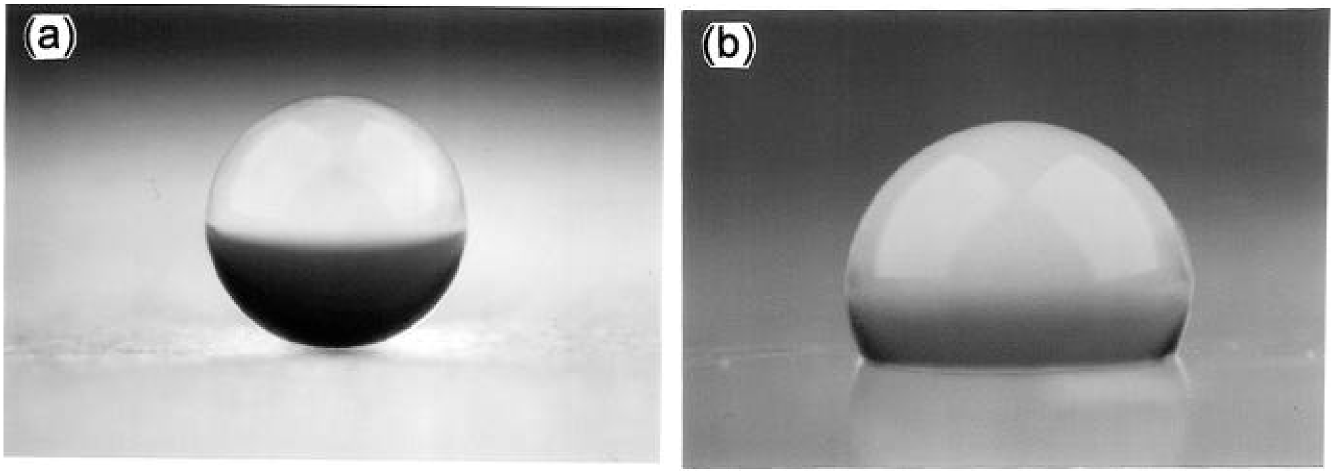

Figure 3. Photographs of water droplets placed on the AKD surfaces: (a) rough surface (the contact angle = 174°); (b) flat surface (the contact angle = 109°).

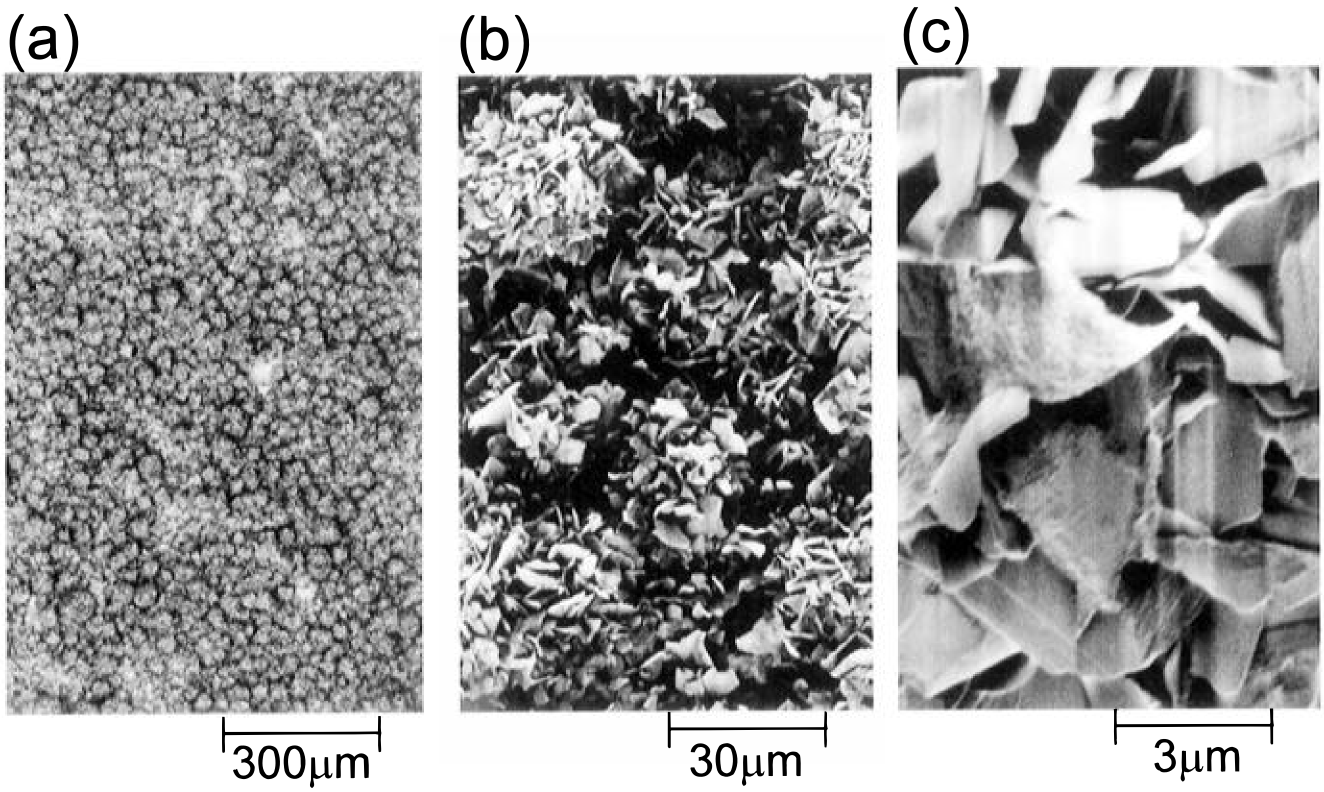

Figure 4. Surface SEM images of a super water-repellent AKD surface at different magnification. The AKD was solidified in a dry N_2 gas atmosphere at room temperature and left standing for curing under the same conditions for 3 days.

is widely used to find a fractal dimension. Self-similarity and the fractal dimension D can be evaluated by the following relationship.[5,6]

$$N(r) \propto r^{-D} \tag{4}$$

where r is the size of boxes, $N(r)$ the number of boxes to cover the object, and D the fractal dimension of the object. The fractal dimension D can be obtained from the slope of the log $N(r)$ vs log r plot.

The box-counting method was applied to three kinds of samples with different mixing ratios of AKD and DAK. The fractal dimension of cross section D_{cross} ($1 \leq D_{cross} < 2$) has been measured by the box-counting method, since the direct measurement of the fractal dimension $D(2 \leq D < 3)$ of the solid AKD surface is difficult. The fractal dimension $D(2 \leq D < 3)$ of the surface has been evaluated as $D \cong D_{cross} + 1$.[7]

Figure 5 shows the SEM images of the cross section of an AKD surface with a magnification of ×150 and ×1500. The SEM magnifications of the photographs were adjusted to each other with a grating replica for a scale standard, because the size of box used in the box-counting measurements depends on the magnification of the SEM images. Trace curves of the solid surface were drawn from the cross sectional SEM images and are shown in Figure 6. The box size r was changed from 0.05 to 320 μm. Figure 7 shows the log $N(r)$ against log r plot for four AKD surfaces with different water-repellency. The slopes of the straight lines give us the fractal dimensions of the surface structures. In the case of AKD/DAK = 10/0, one can see clearly that the straight line has two break points at $r = 0.2$ μm and $r = 34$ μm and two different slopes. One slope is −1.29 between the two critical sizes, and the other is −1 in their outside range. So, the cross section of the surface is fractal with the

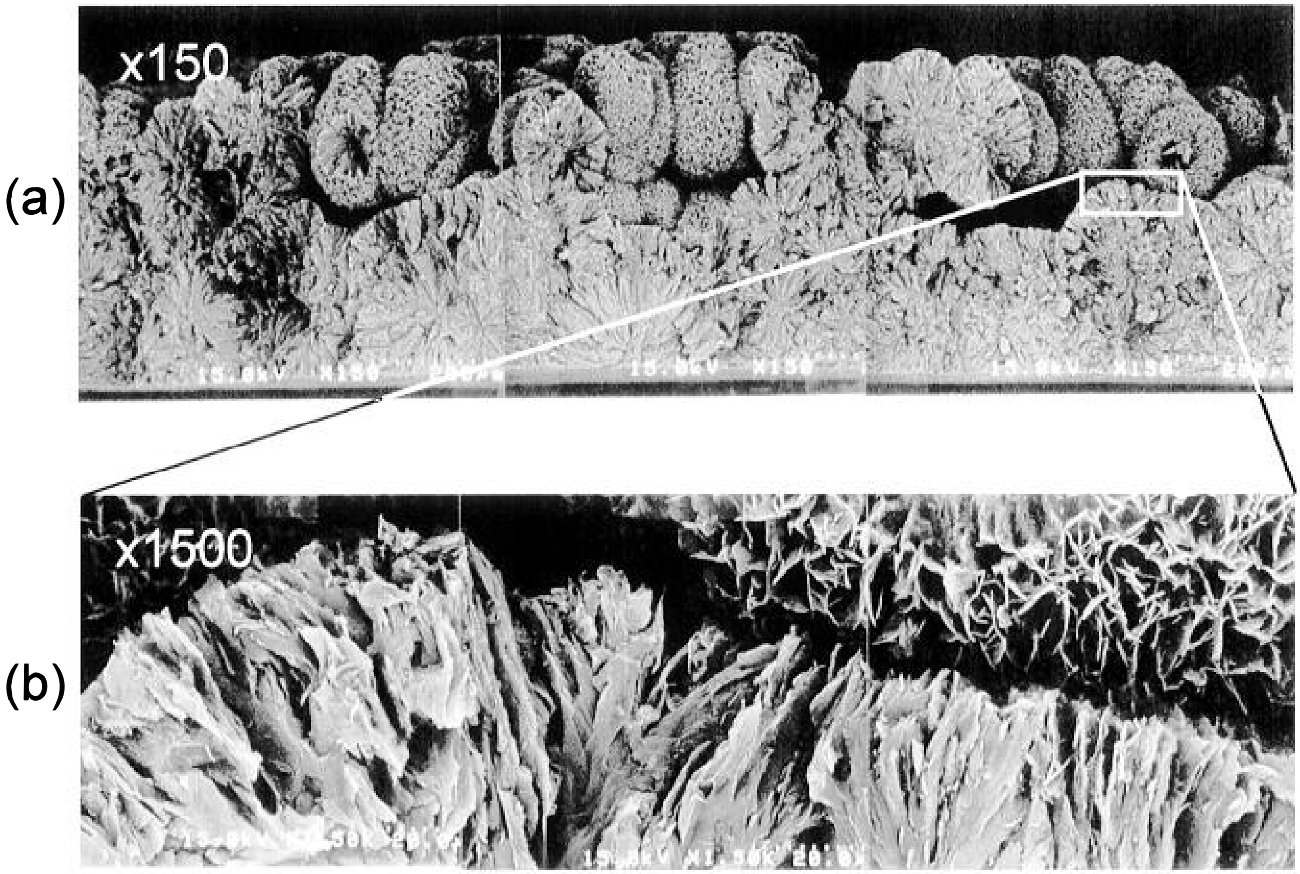

Figure 5. SEM images of the cross section of a super water-repellent AKD surface. Magnifications are ×150 (a) and ×1500 (b).

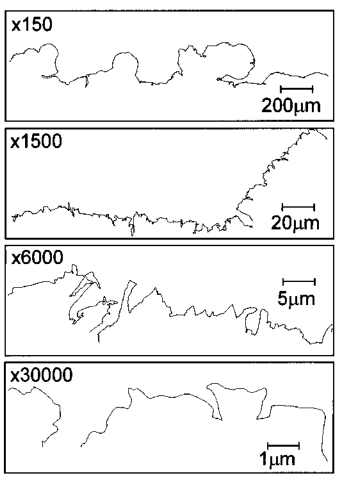

Figure 6. Trace curves of the cross section of a super water-repellent AKD surface. Tracing was made for the SEM photographs shown in Figure 5.

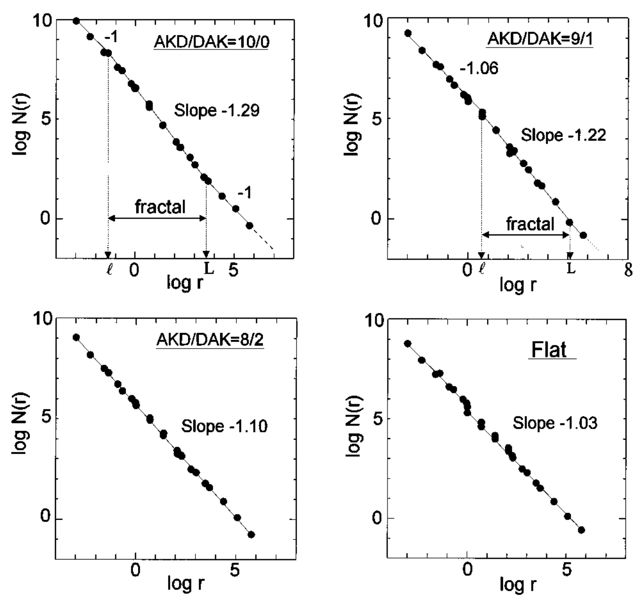

Figure 7. Plots of log $N(r)$ vs log r for the cross sectional trace curves of the flat and the three rough surfaces of AKD. Each plot for rough surfaces shows that the surface is fractal in the range between some limited lengths. The values of L and l could not be detected in the figure of the AKD/DAK = 8/2 since no clear break point was observed. A kink at log $r = 0$ in the figure of the flat surface may appear probably because of the imperfect adjustment of the magnification of the SEM photographs.

dimension of $D_{cross} = 1.29$, and the self-similarity is found to hold between $L = 34\ \mu$m and $l = 0.2\ \mu$m. The fractal dimension of the surface was, then, evaluated to be 2.29.

The fractal analysis was applied to three kinds of samples with different mixing ratios of AKD and DAK. The values of L and l for the sample of AKD/DAK = 8/2 could not be detected unfortunately from Figure 7. The fractal parameters (L, l, D) so obtained for each surface are listed in Table 1. We have found that these surfaces have different fractal parameters. The fractal dimension of the surfaces and also the surface area magnification factor increase with AKD concentration. This behavior corresponds well with the change of contact angle of the water droplet.

3.3. Contact Angles of Liquid on the Flat and Fractal AKD Surfaces. Figure 8 shows the contact angles of water/1,4-dioxane mixtures on the flat and the fractal surfaces of AKD plotted against volume fraction of water. In the case of a flat surface, the contact angle θ of a liquid droplet increases

TABLE 1: Fractal Parameters (L,l,D) and Surface Area Magnification Factor $(L/l)^{D-2}$ for AKD Surfaces Showing Different Water-Repellency

AKD/DAK	L^a/μm	l^b/μm	$D_{surface}$	$(L/l)^{D-2\,c}$	θ_{water}
10/0	34	0.2	2.29	4.43	164−174
9/1	157	1.9	2.22	2.64	156−163
8/2	*d*	*d*	2.10	*d*	126−131
(flat)			2.03	1.00	110

[a] L, upper limit scale of fractal. [b] l, lower limit scale of fractal. [c] $(L/l)^{D-2}$, surface area magnification factor. [d] Data couldn't be determined from Figure 7.

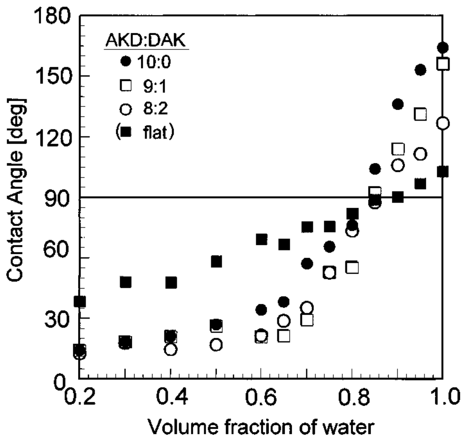

Figure 8. Contact angles of the liquid droplet of water/1,4-dioxane mixtures placed on the AKD solid surfaces plotted against the volume fraction of water in the liquid.

gradually with increasing surface tension γ_L of the liquid. The contact angles θ_f of the fractal surfaces, however, change more abruptly with water concentration, having the same crossing point at ~90°. Wettability of the surface is enhanced by the surface roughness with a boundary of contact angle $\theta = 90°$.

4. Discussion

The contact angle θ_f of a liquid droplet placed on a fractal solid surface is given by eq 5.[2,3]

$$\cos\theta_f = (L/l)^{D-2}\cos\theta \qquad (5)$$

where L and l are the upper and the lower limit lengths of fractal behavior, respectively; $D(2 \le D < 3)$ is the fractal dimension of the solid surface. It is assumed that (1) l is much larger than the diameter of molecules composing a liquid, (2) L is much smaller than the diameter of a liquid droplet, and (3) the interfacial tension of a solid is isotropic, being independent of crystal orientation. The contact angle of a liquid droplet placed on the fractal surface can be changed dramatically when compared with nonfractal surfaces. The surface area magnification factor $(L/l)^{D-2}$ can be estimated experimentally from the $\cos\theta_f$ vs $\cos\theta$ plot, as mentioned in the previous section. The broken line drawn in Figure 9 shows the theoretical expression of eq 5. Applicability of eq 5 is, however, limited. In fact, eq 5 cannot give any contact angle when the absolute value of its right-hand side exceeds unity. A universal expression for θ_f can be obtained by taking account of the adsorption of a gas on the solid−liquid interface and that of a liquid on the solid−gas fractal interface. The behavior of extended theory is also shown in Figure 9 by the thick line. According to the extended theory, the surface area magnification factor should be expressed by the slope at the origin in the $\cos\theta_f$ vs $\cos\theta$ plot.[3]

To verify the theoretical prediction, the relationship between $\cos\theta_f$ and $\cos\theta$ was observed by measuring the wettability of

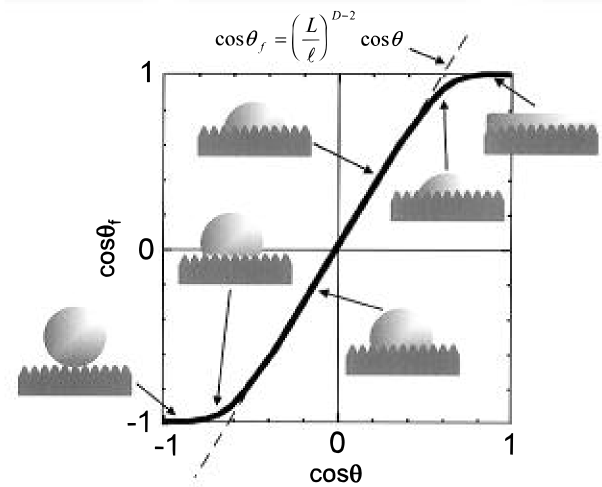

Figure 9. Schematic illustration of the relationship between $\cos\theta_f$ and $\cos\theta$ predicted theoretically.[3] The contact angles of θ and θ_f denote those of some liquid put on the flat and the fractal surfaces.

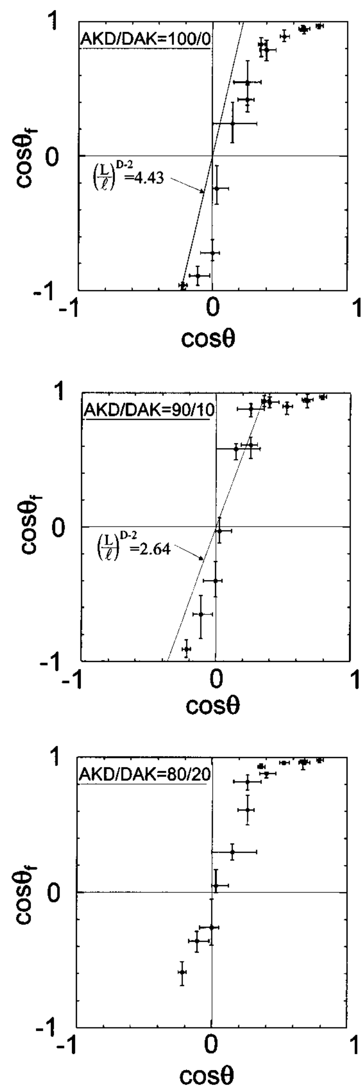

Figure 10. Plots of $\cos\theta_f$ against $\cos\theta$ determined experimentally for the AKD surfaces. The theoretical curves passing through the origin are also drawn by the thin solid straight lines.

the surfaces, changing the surface tension of the sample liquid. The data of contact angles shown in Figure 8 are replotted in the form of $\cos\theta_f$ against $\cos\theta$ (Figure 10). The straight lines of $\cos\theta_f$ against $\cos\theta$ having the surface area magnification factor $(L/l)^{D-2} = (34/0.2)^{2.29-2} \cong 4.43$ and $= (157/1.9)^{2.22-2} \cong$

2.64 calculated from fractal parameters listed in Table 1 are also drawn by the thin solid lines in Figure 10. The surface area magnification factor evaluated from the fractal parameters agrees well with the slope of the experimental data of the wettability.

The fractal theory for the wetting phenomena of a solid surface was verified experimentally by the contact angle measurements of a liquid droplet and the fractal analysis of the surfaces being done independently. However, each plot does not pass through the original point (0,0), presumably because the exact equilibrium of contact angle of the liquid droplets is not established on the rough surfaces.

5. Conclusion

The AKD forms spontaneously an extremely rough surface by solidification from the melted state. The surface structure of the AKD solid was confirmed to be a fractal by box-counting measurements. A super water-repellent surface ($\theta_f = 174°$) was obtained utilizing this fractal surface without any fluorination treatments. The theory of the wetting phenomena of a fractal surface was verified experimentally by the cos θ_f vs cos θ plot.

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