# Icephobic Coating through a Self-Formed Superhydrophobic Surface Using a Polymer and Microsized Particles

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Cite This: https://doi.org/10.1021/acsami.1c22404 **Read Online** ACCESS III Metrics & More Article Recommendations s Supporting Information ABSTRACT: Icephobic coatings have been extensively studied for decades to overcome the potential damage associated with ice SiO<sub>2</sub>/PDMS-PVDF coating formation in various devices that are operated under harsh weather conditions. Superhydrophobic surface coatings have been applied for icephobic coating applications owing to their low surface energy. In this study, an icephobic coating of a self-formed superhydrophobic surface using polydimethylsiloxane (PDMS) and SiO<sub>2</sub> powder was Substrate investigated. The effect of superhydrophobicity on icephobicity was determined by varying the experimental parameters. Polyvinylidene fluoride (PVDF) was added to the PDMS solution to improve the Large-area application mechanical properties of the icephobic layer. The PDMS-PVDF in a very simple way solution also showed a self-formation behavior into a super-

the multilevel nanostructure formed by physical and chemical interactions between the mixture and  $SiO_2$  powder. We believe that the proposed approach will be a suitable candidate for various practical applications of icephobicity and a model system to understand the correlation between superhydrophobicity and icephobicity.

KEYWORDS: superhydrophobic, icephobic, polydimethylsiloxane, SiO<sub>2</sub> powder, polyvinylidene fluoride, ice adhesion, roughness

# 1. INTRODUCTION

In infrastructure applications and devices that are used at or below 0 °C, the formation of ice can result in critical safety issues and severe operational damages.<sup>1–3</sup> Conventionally, mechanical methods, such as heating and scrapping, or chemical treatments, such as anti-freeze solutions and salts, have been employed as anti-icing and de-icing methods.<sup>4</sup> However, these methods are inefficient, time-consuming, expensive, and/or harmful to the environment. An icephobic surface is defined as a surface that prevents ice nucleation or has low adhesion strength (<100 kPa) to ice.<sup>5</sup> An effective way to overcome the problems associated with the abovementioned methods is to coat the desired surface with an icephobic material. The development of passive icephobic surfaces and coatings has attracted significant research attention, which allow ice removal by natural forces such as wind and gravity to prevent ice accumulation.

hydrophobic surface. In addition, the icephobicity and mechanical properties of the PDMS-PVDF mixture coating improved because of

Icephobicity prevents heterogeneous nucleation of ice on the surface and minimizes the adhesion force between the ice and surface.<sup>6</sup> Both these processes are strongly related to hydrophobicity determined by the surface energy difference between water and the surface.<sup>7–9</sup> Heterogeneous nucleation of ice is difficult on a low-energy surface; ice has a low contact area with the surface that results in a low adhesion force. Therefore, several icephobic coating studies have been conducted based on

the fabrication of superhydrophobic surfaces.<sup>10–12</sup> In particular, hydrophobic polymers with low surface energy and high mechanical properties, such as polytetrafluoroethylene (PTFE), have been selected as materials for superhydrophobic and icephobic coatings.<sup>13</sup> Furthermore, superhydrophobic surfaces have been fabricated using various methods, such as modified nanoparticles,<sup>14</sup> etching,<sup>15–17</sup> sputtering,<sup>13</sup> chemical vapor deposition (CVD),<sup>18</sup> and lithography,<sup>19</sup> among others,<sup>20–24</sup> also have been applied to icephobic surfaces, as shown in Table 1. These approaches maximize the surface roughness on a superhydrophobic surface by reducing the physical contact area due to the existence of "trapped air" between the surface and water/ice based on the Cassie–Baxter model. However, these methods are costly and complex, have low durability, and are limited to large-area coatings, which limit their further applications.

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Table 1.	. Comparison	n of Current	Work to	Relevant	Earlier	Studies
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materials	method	temperature (°C)	ice adhesion (kPA)	refs
PDMS, PVDF, SiO <sub>2</sub> powder	scattering powder on the PDMS, PVDF solution	-35	46	this work
Al, PTFE, Teflon	RF sputtering of PTFE or Teflon on the rough Al surface	-10	72	13
TEOS-GLYMO, PFOTES, SiO <sub>2</sub> powder	modification of $SiO_2$ powder through a polymer coating	-10	50	14
Al, PFES	coating a cross-linked PFES on the etched Al surface	-10	200	15
Al, POTS, SiO <sub>2</sub> powder	POTS coating on $SiO_2$ powder through CVD	-10	100	18

Polydimethylsiloxane (PDMS) is the most widely studied material owing to its low ice adhesion and anti-icing properties that result from its low surface energy, hydrophobicity, viscoelasticity, nontoxicity, low cost, and ease of use. Recently, we developed an efficient and one-step cost-effective method for preparing superhydrophobic surfaces using PDMS and SiO<sub>2</sub> powders.<sup>25</sup> When the SiO<sub>2</sub> powder was sprinkled on PDMS, it was spontaneously coated by PDMS through the biscuit dunking effect described by Washburn's equations and Stokes' law. The water contact angle (WCA) of the coatings was as high as  $150^\circ$ , and the water sliding angle (WSA) was below  $21^\circ$ . This spontaneous coating mechanism and superhydrophobicity make it a good candidate for icephobicity. Although a superhydrophobic surface is easily formed even on a curved surface, the correlation between icephobicity and superhydrophobicity of the layer has not yet been studied. In addition, the inherent disadvantages of PDMS, such as low adhesion and mechanical durability, have not been studied and evaluated under icing conditions that typically have mechanically harsh environments.

In this study, we employed the spontaneous coating method using PDMS and SiO<sub>2</sub> powders for icephobic applications. The powder size was varied using ball milling, and the formation of porous 3D micro/nanostructures was investigated as a function of the powder size. Polyvinylidene fluoride (PVDF) was added to improve surface adhesion, mechanical durability, and icephobicity. PVDF is a polymer already being exploited to form superhydrophilic and superoleophobic surfaces.<sup>26,2</sup> However, in this study, it has been established that PVDF can also be used in superhydrophobic and icephobic fields. Surface morphology, chemical composition, and hydrophobicity were investigated using field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), and WCA measurements. We believe that this study will provide help us understand the correlation between hydrophobicity and icephobicity.

#### 2. EXPERIMENTAL METHODS

2.1. Superhydrophobic/Icephobic Coating. Sandblasted stainless steel 304 (SS, Three Steel,  $20\times20\times8$  mm) was used as the substrate. The substrate was cleaned using sequential processes with ultrasonication in acetone, isopropyl alcohol, and deionized (DI) water. The remaining water was blown off with nitrogen gas and then vaporized in an oven for 5 min at 80 °C. The PDMS coating solution was made with Sylgard 184 base and a curing agent (Dow Corning) in 10:1 weight ratio and evenly hand-mixed for 3 min. The bubbles formed during mixing were removed by placing them in a vacuum desiccator for 20 min. Thereafter, 0.4 g of PDMS solution was dropped onto the SS substrate and spin-coated for 5 s at 100 rpm and then for 60 s at 800 rpm. After the PDMS solution was uniformly coated, SiO<sub>2</sub> powder (Sigma-Aldrich, average powder size of 5.4  $\mu$ m, irregular shape) was sprinkled using a 200-mesh sieve to cover the substrate uniformly. The sample was then placed at room temperature (24  $^\circ C$  and 60% humidity) for 10 min to promote the self-formation process of PDMS and SiO<sub>2</sub> powder as described in our previous paper.<sup>25</sup> The SiO<sub>2</sub>/ PDMS-coated substrate was baked in an oven at 80 °C for 3 h for

curing, and the unreacted  $\mathrm{SiO}_2$  powder was removed by nitrogen blowing.

To improve the adhesion and mechanical properties of the  $SiO_2/$ PDMS coating, PVDF solution was added to the PDMS solution. The PVDF solution was prepared by dissolving 1-part PVDF powder (Sigma-Aldrich) in 4-part dimethylacetamide (DMAc) (Sigma-Aldrich) by weight and mixed into the PDMS solution. The resulting mixture was spin-coated onto the SS substrate under the same conditions as before, and the SiO<sub>2</sub> powder was sprinkled on it. The sample was cured at 160 °C and 60% humidity for 3 h on a hot plate. Solvents and DMAc were fully vaporized during the curing period, which resulted in the formation of a composite coating layer of PDMS and PVDF with SiO<sub>2</sub> powder. X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe II, ULVAC-PHI) was performed to identify the surface elements of the SS substrate, and X-ray diffraction (XRD, SmartLab, Rigaku) and Fourier transform infrared (FT-IR, VERTEX 80V, Bruker) analyses were performed to confirm the phase of PVDF. SiO<sub>2</sub> powders with different diameters were prepared using a ball milling machine (PM100, Retsch) using a 6.25 mm zirconia ball for 30 min, 1, 3, and 10 h at 350 rpm, and the original diameter of 5.4  $\mu$ m was reduced to 5.1, 2.9, 1.9, and 1.3  $\mu$ m, respectively (Figure S1 of the Supporting Information). The average diameter of these SiO<sub>2</sub> powders was measured using a particle size analyzer (LS13 320MW, Beckman Coulter and Microtrac Ztrac, Microtrac).

**2.2.** Surface Morphology Analysis. FE-SEM (JSM-7001F, JEOL) and thermal SEM (VEGA3 SBH, Tescan) were used to analyze the micro/nanoscale morphology of the coating surface formed with different sizes of SiO<sub>2</sub> powders. Since PDMS, PVDF, and SiO<sub>2</sub> are electrically insulating, platinum sputtering was used to avoid charging. EDS (JSM07001F) was used to analyze the elemental mapping of the coating surface. The root mean square (rms) surface roughness was analyzed through a surface profiler (DEKTAK XT-E, Bruker, 1 Å vertical resolution). The rms surface roughness was calculated as the average roughness of the porous 3D micro/nanostructure peaks and valleys.

2.3. Hydrophobicity and Icephobicity Analysis. The static WCA and dynamic WCA on the coating surface were analyzed by WCA measurements (SDL200TEZED, Femtobiomed). Each contact angle was measured using 7-10  $\mu$ L of DI water droplets. The ice for measuring ice adhesion was obtained by putting 2 mL of DI water in a plastic cuvette  $(10 \times 10 \times 40 \text{ mm})$ , flipping it over the sample surface, and freezing it at -15 °C for 6 h (Figure S2 of the Supporting Information). The plastic cuvette was then removed so that the contact area between the coated sample surface and the ice was 1 cm<sup>2</sup>. After removing the cuvette, the sample was frozen for an additional 6 h at -15°C. Samples with the attached ice were transferred to an ice chamber (details given below) within 5 s. The ice adhesion was measured after 5 min of loading on the surface of the cold Peltier plate (Oriental Matrix, TECI-12706) inside the ice chamber. The icephobic adhesion experiment was conducted in a lab-built ice chamber, which was set up with an aluminum profile by modifying the inside of the refrigerator. The left side of the ice chamber had a push-pull gauge that measured the ice adhesion, while the right side consisted of a pneumatic cylinder that held the sample, Peltier plates, and water coolers (Figure S3 of the Supporting Information). The temperatures for the ice adhesion test were maintained at -35 and 0 °C for the cold Peltier plate and chamber, respectively. Humidity was maintained at 45% ( $\pm$ 5%). The adhesion force was measured until the ice fell off by pushing the push-pull gauge with a pneumatic cylinder. Data from the push-pull gauge were acquired every 50 ms using ZLINK3 software (Imada). Ice adhesion



Figure 1. Surface SEM images of SS (a), PDMS/SS (b), and SiO<sub>2</sub>/PDMS/SS (c). rms roughness (d) and hydrophobicity (WCA, WSA) (e) and ice adhesion strength (f) of each surface.

was obtained by dividing the force applied by the contact area between the ice and the surface, as shown in the following equation

$$\tau = \frac{F}{A},\tag{1}$$

where  $\tau$  is the ice adhesion (kPa), *F* is the force measured until the ice detaches (N), and *A* is the contact area between the ice and the surface (m<sup>2</sup>).

**2.4. Coating Adhesion and Tensile Strength Analysis.** A bare polymer coating without powder was used to evaluate the properties of the polymer. For adhesion analysis, a 60-mesh copper sieve was applied onto the polymer solution when the polymer was cured (Figure S4 of the Supporting Information). The copper mesh was then pulled in the opposite direction to remove the coating, and the adhesion between the coating and the SS substrate was measured using a high-precision micromechanical test instrument (QM100S, QMESYS). In addition, the tensile strength of the coating was measured using a universal testing machine (WL2100, Withlab). The size of the sample used for tensile strength analysis was  $40 \times 10$  mm, and the thickness was less than 0.2 mm.

# 3. RESULTS AND DISCUSSION

Figure 1a–c shows the surface morphologies of sandblasted bare SS, uniformly spin-coated PDMS surface, and SiO<sub>2</sub>/PDMS coating, respectively. The WCAs of each surface are shown in the inset in the FE-SEM images. The surface morphology of the SS substrate without any coating appears relatively flat with cracks from the sandblasting treatment (Figure 1a). After the PDMS coating, the surface becomes smooth (Figure 1b). By adding SiO<sub>2</sub> powder, the surface morphology changes significantly and becomes rougher (Figure 1c). Figure 1d shows the SS substrates without and with the PDMS coating with low rms roughness values of 62.3 and 4.71 nm, respectively. However, the rms roughness of the SiO<sub>2</sub>/PDMS surface was

1.94  $\mu$ m, which is approximately 411 times higher than that of the PDMS-only surface. Figure 1e shows the WCA and WSA of the three surfaces. Water wettability is known to significantly depend on the surface energy and the surface roughness.<sup>28</sup> The WCA of the SS substrate without PDMS was 85.7°; however, the WSA was greater than  $90^{\circ}$ . The  $90^{\circ}$  angle is the maximum value that the WSA can reach, and while measuring the WSA of the SS surface, the water droplets did not fall when the SS surface was tilted to 90°. This indicates that the WSA of the SS surface was above 90°. In contrast, a small WSA of 33.8° was measured on the PDMS-coated SS surface with a WCA of 116.1°. This hydrophobic behavior is due to the low surface energy (22.1 mJ/ m<sup>2</sup>) of PDMS.<sup>29</sup> The WCA on the SiO<sub>2</sub>/PDMS/SS surface was measured as 150°, with a WSA as low as 21°. The high rms roughness, high WCA, and low WSA of the SiO<sub>2</sub>/PDMS/SS can be explained by the surface energy and the change in the contact area between the water droplet and surface (eq 2).<sup>30–33</sup>

$$\cos\theta^{\rm CB} = f \,\cos\theta_{\rm eq} - (1 - f),\tag{2}$$

where f is the fraction of the contact area between the water droplet and surface,  $\theta$ CB is the WCA of the Cassie–Baxter surface, and  $\theta$ eq is the WCA of the flat smooth surface. In addition, f was reduced from 1 to 0.24 at WCAs of 116.1 and 150.0° when SiO<sub>2</sub> powder was added. The reduction in f indicates that the physical contact area was decreased by increasing the air trapped between the water droplet and the surface. Therefore, the interaction between the water droplet and the surface becomes smaller, leading to a decrease in surface adhesion and a smaller WSA.

As mentioned in the Introduction, superhydrophobic surfaces with low surface energy and high surface roughness have a huge potential for icephobicity. The ice adhesion strengths of the bare



Figure 2. Hydrophobic (WCA, WSA) (a), rms roughness and ice adhesion strength (b), and surface SEM images of SiO<sub>2</sub>/PDMS/SS coatings depending on SiO<sub>2</sub> powder size (c).

SS, PDMS/SS, and SiO<sub>2</sub>/PDMS/SS surfaces were measured as 361.6, 209.8, and 151.5 kPa, respectively. When ice forms on the SS surface, the polar metal oxide functional groups increase the electrostatic interactions between ice and the surface, resulting in higher ice adhesion strength.<sup>34,35</sup> Polar metal oxide bonding on the SS surface is confirmed by XPS (Figure S5 of the Supporting Information).<sup>36–42</sup> For PDMS/SS, the electrically nonpolar CH<sub>3</sub> ligand has less electrostatic interaction with ice, and thus, the ice adhesion strength is reduced.<sup>43</sup> In addition, the ice adhesion strength of SiO<sub>2</sub>/PDMS/SS is further reduced owing to the decrease in the contact area.

Hydrophobicity and icephobicity can be improved by changing the surface morphology, that is, by reducing the contact area. The SiO<sub>2</sub> powder size was controlled by ball milling, and hydrophobicity and icephobicity were evaluated for powder sizes of  $1.3-5.4 \ \mu$ m. Figure 2a shows the WCA and WSA of SiO<sub>2</sub>/PDMS surfaces with powder sizes varying from 1.3 to 5.4  $\mu$ m. The WCA was measured to be 161, 159, 155, 152, and 150° for powder sizes of 1.3, 1.9, 2.9, 5.1, and 5.4  $\mu$ m, respectively. The WSA increased from 6° for 1.3  $\mu$ m powder to up to 21° for 5.4  $\mu$ m powder. Using eq 2, we calculated the fraction of the contact area (f) for the 1.3  $\mu$ m powder sample as 0.091, while that of the 5.4  $\mu$ m sample was 0.24. Therefore, the low WSA for the smaller SiO<sub>2</sub> powder can be attributed to the smaller contact area between the coating layer and the water droplet.

To further understand the correlation between powder size and superhydrophobicity/icephobicity, the roughness was measured. Figure 2b shows plots of the surface roughness and the ice adhesion strength versus the SiO<sub>2</sub> powder size. The rms roughness decreases rapidly with increasing the powder size from 1.3 to 5.4  $\mu$ m. rms roughness of the surface with the smallest powder size (1.3  $\mu$ m) is 3.72, which is two times higher than that with the largest powder size (5.4  $\mu$ m). In addition, the ice adhesion strength increases with increasing the powder size. For the 1.3  $\mu$ m powder sample, ice adhesion strength was 94 kPa, which increased to 93, 104, 136, and 152 kPa for 1.9, 2.9, 5.1, and 5.4  $\mu$ m powder samples, respectively. The surface roughness and ice adhesion strength are inversely proportional to each other. Figure 2c shows the surface morphology of SiO<sub>2</sub>/PDMS with different powder sizes. Although it is difficult to quantify them, the density of powder exposed over the surface and the surface roughness are likely to decrease with increasing the powder size, from left to right in Figure 2c. The porous 3D micro/nanostructures formed by finer and smaller SiO<sub>2</sub> powders are more favorable to increased trapped-air layers, <sup>14,44</sup> thus reducing the surface contact area with water/ice and resulting in an improvement in the superhydrophobicity and anti-icing properties.

The changes in the surface roughness and density were investigated based on the formation mechanism of the  $SiO_2/PDMS$  layer. As reported in our previous paper,<sup>25</sup> there are two comparative interactions between the PDMS layer and  $SiO_2$  powder. When  $SiO_2$  powder is sprinkled on the PDMS solution, the PDMS solution penetrates the  $SiO_2$  powders governed by the Washburn equation (eq 3) and the  $SiO_2$  powder sediments into the PDMS solution by Stokes' law (eq 4). The Washburn equation is as follows

$$L = \sqrt{\frac{\gamma r t \cos \theta}{2\mu}},\tag{3}$$

where *L* is the penetration length  $(\mu m)$ ,  $\gamma$  is the surface tension of PDMS (mJ/m<sup>2</sup>), *r* is the pore radius  $(\mu m)$ , *t* is the time (s),  $\mu$  is the dynamic viscosity (Pa s), and  $\theta$  is the contact angle (°) between the liquid and the solid. Furthermore, Stokes' law is given as follows

$$\mathbf{v} = \left[\frac{\rho_{\rm s} - \rho_{\rm l}}{18\mu}g\right]D^2,\tag{4}$$

where  $\nu$  is the velocity of the SiO<sub>2</sub> powder sinking (m/s),  $\rho_s$  is the mass density of the SiO<sub>2</sub> powder (g/cm<sup>3</sup>),  $\rho_1$  is the mass



**Figure 3.** Behavior of SiO<sub>2</sub> and PDMS according to the SiO<sub>2</sub> powder size (5.4 and 1.3  $\mu$ m) and time in the manufacturing process of the SiO<sub>2</sub>/PDMS/SS sample. Each powder was sprinkled on the PDMS (a, e), and after 1 s, PDMS coated all SiO<sub>2</sub> powders (b, f). After 10 min, the unreacted SiO<sub>2</sub> powder was removed by nitrogen blowing to form a rough surface (c, g). After a curing time of 3 h, the surface roughness was determined by the size of the SiO<sub>2</sub> powder (d, h).

density of the PDMS solution  $(g/cm^3)$ , *g* is the gravitational field strength (9.8 m/s<sup>2</sup>),  $\mu$  is the dynamic viscosity (Pa s), and *D* is the diameter of the SiO<sub>2</sub> powder ( $\mu$ m).

As shown in Figure 3a-h, when the SiO<sub>2</sub> powders were sprinkled on the PDMS surface, they sink into the PDMS solution, while PDMS penetrates the capillaries formed by the vacant spaces between the powder particles. For the 5.4  $\mu$ m SiO<sub>2</sub> powder, the penetration length, L, was calculated over time using eq  $2^{25}$  assuming that the shape of the SiO<sub>2</sub> powder is spherical,  $\gamma$  is 22.1 mJ/m<sup>2</sup>,  $\mu$  is 3.5 Pa s, r is 1  $\mu$ m, and  $\theta$  is 0°. Furthermore, 1 s after SiO<sub>2</sub> is sprinkled on the PDMS solution, the PDMS solution penetrates 56.2  $\mu$ m under capillary action and covers all SiO<sub>2</sub> powder. In addition, 1.3  $\mu$ m SiO<sub>2</sub> powder is about four times smaller than the 5.4  $\mu$ m powder, and the pore size is reduced by the same ratio. Based on Washburn (eq 3), when the pore size is reduced four times, the penetration length over time is reduced two times. Hence, when compared to 5.4  $\mu$ m SiO<sub>2</sub> powder, the penetration length for the 1.3  $\mu$ m SiO<sub>2</sub> powder sample is 28.1  $\mu$ m.

However, for SiO<sub>2</sub> powder sinking, when the powder size is reduced four times, the sinking rate is decreased 16 times, as per Stokes' law (eq 4). For calculating the sinking rate, it was assumed that the velocity of the SiO<sub>2</sub> powder sinking,  $\nu_1$  is unaffected by the weight of the stacked powder; the mass density of SiO<sub>2</sub> powder and PDMS was 2.65 and 0.965 g/cm<sup>3</sup>, respectively, and dynamic viscosity was 3.5 Pa s, for D of 5.4 and 1.3  $\mu$ m. The calculated sinking velocity of SiO<sub>2</sub> powder of 5.4 and 1.3  $\mu$ m powder was 7.6 and 0.44 nm/s, respectively. These rates are very small compared to the penetration rate of the PDMS solution. Thus, at the beginning, PDMS penetrates SiO<sub>2</sub> powders and covers most of them quickly, and the SiO<sub>2</sub> powder sinks into the PDMS layer during the subsequent curing process. The sinking depth is much greater for the larger SiO<sub>2</sub> powders, and they are confined in the PDMS layer (Figure 3d), but the smaller SiO<sub>2</sub> powders retain their original rough morphology (Figure 3h). In the real case, when the  $SiO_2$  powder was sprinkled, it was randomly stacked, so that the penetration of PDMS was partially limited by eq 3 due to the reduction in pore size of the SiO<sub>2</sub> powder in areas with denser powder stacking. After the uncovered powder is blown away with N<sub>2</sub>, the surface of the smaller SiO<sub>2</sub> powder might have a rougher surface morphology. Therefore, the smaller SiO<sub>2</sub> powder shows higher

roughness and surface density on the PDMS layer compared to the larger  $SiO_2$  samples, resulting in low ice adhesion strength due to the reduced contact area.

Since icephobic coatings are applied to the surfaces exposed to extreme weather conditions, such as heavy snow and cold, their mechanical durability is crucial. In addition, the typical adhesion strength of ice on a normal surface is high, and hence, the adhesion of the icephobic layer to the surface should be durable under multiple de-icing processes. However, PDMS has relatively weak mechanical properties. Therefore, various studies have been conducted to improve the mechanical properties of PDMS, especially by adding PVDF to PDMS.<sup>45–47</sup> To thoroughly understand the mechanical properties, PVDF was mixed with PDMS in different proportions. Figure 4 shows the change in contact angles between the liquid PDMS–PVDF solution and the SiO<sub>2</sub> wafer with time and PDMS–PVDF weight ratios. For samples with PDMS–PVDF ratios of 9:1 and



**Figure 4.** Change of the contact angle between the SiO<sub>2</sub> wafer and PDMS–PVDF solution according to time and the PVDF content.



Figure 5. rms surface roughness (a), WCA (b), WSA (c), and ice adhesion strength (d) of SiO<sub>2</sub>/PDMS-PVDF/SS according to the PVDF content.

7:3, the liquid failed to form a sphere and showed irregular shapes. In the previous report,<sup>45</sup> DMAc, the solvent for PVDF, is shown to chemically react with PDMS, resulting in increased viscosity. Due to this increased viscosity, an accurate contact angle could not be measured and the PDMS-PVDF solution was not uniformly coated during the spin-coating process. For weight ratios over 7:3, it would be difficult for the PDMS-PVDF solution to penetrate SiO<sub>2</sub> powder. When the weight ratio was reduced to 5:5, the contact angle was measured as 34.1° at 5 s, which decreased to  $13^{\circ}$  after 600 s. The contact angles further decreased from 31.3 to  $20.4^{\circ}$  and from 21.5 to  $16.4^{\circ}$  for the 3:7 and 1:9 samples, respectively. The low contact angle for the liquid PDMS-PVDF solution on the SiO<sub>2</sub> wafer indicates that the SiO<sub>2</sub> surface has a high surface energy with the PDMS-PVDF solution and can thus be coated uniformly as confirmed by FE-SEM and EDS analyses (Figure S6 of the Supporting Information).

The superhydrophobicity, icephobicity, and surface roughness of the coatings formed with different weight ratios of PDMS-PVDF were analyzed. Figure 5a shows the rms roughness of the coatings with different weight ratios of PDMS–PVDF and increasing powder size from 1.3 to 5.4  $\mu$ m. rms roughness was reduced from 3.85  $\mu$ m for the 1.3  $\mu$ m SiO<sub>2</sub> powder sample to 1.65  $\mu$ m for the 5.4  $\mu$ m powder sample. The roughness trend remained almost similar for all the coatings with all weight proportions except for the 1:9 sample. For the 1:9 coating, the rms roughness was slightly higher than that of the other coatings, probably due to the higher content of PVDF. Roughness showed a typical inversely proportional curve with increasing the powder size (Figure 2). The surface roughness for each proportion and different sizes of powder coatings are further shown using FE-SEM (Figure S8 of the Supporting Information).

Figure 5b shows the WCA behavior with increasing the powder size for coatings with different PDMS-PVDF weight ratios. For the PDMS-only surface, the WCA decreased from 161 to 150° for the 1.3 and 5.4  $\mu$ m-sized powder-coated surfaces, respectively. However, with an increase in the PVDF content in the PDMS solution, the WCA decreased insignificantly. For all the ratios, the WCA decreased from 160 to 158° from the 1.3 to 5.4  $\mu$ m-sized powder-coated surfaces. This indicates that the addition of PVDF to PDMS not only improves the mechanical properties but also adds to the superhydrophobic properties. Furthermore, the WSA was measured, and the results showed a similar trend (Figure 5c). With increasing powder size, the WSA increased for all surfaces. However, compared to the PDMS-only surface, the WSAs of the PDMS-PVDF surface showed lower values for all the powder sizes. The WSA remained less than  $10^\circ$  for the 5:5 mixture coating and less than 15° for the coating with 3:7 weight ratio of PDMS-PVDF.

The ice adhesion strength was measured and compared to that of the PDMS-only coated surface (Figure 5d). With increasing the powder size, ice adhesion showed an overall increasing trend because the micro/nanoscale roughness was reduced, leading to an increase in the contact area of the ice/ water droplet on the surface. With the addition of PVDF, the trend remains the same; however, the ice adhesion strength becomes lower than that of the PDMS-only surface. For all the ratios, ice adhesion remained almost similar and increased from 46 to 113 kPa for the 1.3–5.4  $\mu$ m powder sample surfaces. The lowest ice adhesion was 46 kPa, which is comparable to the values on icephobic coatings reported so far.<sup>48–51</sup>

The change in the surface morphology with the addition of PVDF was studied. For quantification, 5  $\mu$ m homogeneous spherical SiO<sub>2</sub> powder was used (Figure 6a), instead of the



**Figure 6.** Bare  $SiO_2$  powder (a) and  $SiO_2$  powder surface change in the  $SiO_2/PDMS-PVDF$  coating according to PVDF content (b-f). The schematic diagram of the curing process of PDMS (g) and PDMS-PVDF coatings (h).

irregularly shaped powders. Figure 6b,c shows FE-SEM images of SiO<sub>2</sub>/PDMS/SS and SiO<sub>2</sub>/PDMS-PVDF (5:5)/SS, respectively. The PDMS and PDMS-PVDF solutions seem to fully cover the SiO<sub>2</sub> powder particles. However, with increasing the PVDF content in the solution, very small particles were observed on the 5  $\mu$ m SiO<sub>2</sub> powder (Figure 6d–f). When PVDF is cured at a relatively high humidity, vapor-induced phase separation occurs, leading to agglomeration of PVDF and formation of a nonpolar  $\alpha$ -phase crystal.<sup>52,53</sup> In our experiments, dominant formation of the nonpolar  $\alpha$ -phase with a minor polar  $\beta$ -phase was observed in XRD and FT-IR analyses (Figure S7 of the Supporting Information).<sup>54-63</sup> As the PVDF concentration increased, the amount of PDMS between the SiO<sub>2</sub> powders decreased and the nonpolar  $\alpha$ -phase crystal of PVDF increased. Figure 6g,h illustrates the differences between the SiO<sub>2</sub>/PDMS/ SS- and SiO<sub>2</sub>/PDMS-PVDF/SS-coated and -cured surfaces. The SiO<sub>2</sub>/PDMS-PVDF/SS sample has improved hydrophobicity and icephobicity compared to those of the SiO<sub>2</sub>/ PDMS/SS sample because of the decrease in PDMS between SiO<sub>2</sub> powders and the increase in nanoscale roughness caused by the nonpolar  $\alpha$ -phase PVDF crystal on the surface of the SiO<sub>2</sub> powder.<sup>54–56</sup> Nanoroughness can reduce the interaction with water/ice by forming an air layer trapped between the surface and water/ice.

As described in the Introduction, icephobic coatings are exposed to harsh conditions, such as strong winds and cold weather. Therefore, the mechanical properties of the coating are important, and a strong adhesion between the icephobic coating and the substrate is necessary. Figure 7a shows the change in tensile strength of the PDMS, PVDF, and PDMS-PVDF coatings. Bare PDMS has a high strain of 46% and tensile strength of 0.9 MPa. However, bare PVDF has a low strain of 1.5% but a high tensile strength of 4.8 MPa. As the PVDF ratio increased, the strain decreased and the tensile strength increased because the strength of PVDF is higher than that of PDMS. Figure 7b shows the peel-off results for the adhesion of each coating on the SS substrate. For the PDMS-only sample, a force of 43 gf/mm was required to peel off the PDMS coating from the SS substrate. As the PVDF content increased, the adhesive force increased. The 5:5-ratio sample showed the highest adhesion at 337 gf/mm. In the cases of 3:7 and 1:9, the adhesion was 119 and 133 gf/mm, respectively. The adhesive force between the coating and the substrate depends on both internal electrical and mechanical forces.<sup>64,65</sup> The higher adhesion force of the 5:5 sample than that of the PDMS-only sample can be explained by the electrical interfacial force.<sup>54</sup> Compared to the PDMS coating that has a nonpolar CH<sub>3</sub> ligand, the polar  $\beta$ -phase is formed in the PDMS-PVDF coating, and thus, a strong electrical bonding with metal oxide of the SS substrate adhesion is generated.<sup>66,6</sup>



**Figure 7.** Tensile strength (a) and adhesion to the substrate (b) of the PDMS–PVDF coating according to the PVDF content. The schematic of the weakening of adhesion of the PDMS–PVDF coating (c).

However, when the PVDF ratio increases further, the adhesive force decreases again in 3:7 and 1:9 samples. The shrinkage rate of PDMS is approximately 2% during the curing process, while PVDF shows a large shrinkage rate of approximately 40%.<sup>68,69</sup> Larger shrinkage with a higher PVDF ratio leads to a reduction in the contact area between the coating and substrate (Figure 7c). Therefore, the adhesion forces are lower for samples with high PVDF ratios.

#### 4. CONCLUSIONS

In this study, we applied a superhydrophobic coating formed by the spontaneous formation method of SiO<sub>2</sub>/PDMS and investigated the effects of superhydrophobicity on icephobicity based on the surface roughness of the coating. When the sizes of SiO<sub>2</sub> powders were changed, the surface morphology changed, as explained by the penetration of the polymer solutions and sedimentation of SiO<sub>2</sub> based on Washburn's equation and Stokes' law. The roughness of the SiO<sub>2</sub>/PDMS coating obtained using smaller powders is higher, and the hydrophobicity and icephobicity increase. PVDF was added to the PDMS solution to improve the mechanical properties, such as tensile strength and adhesion to substrates. The addition of PVDF to PDMS showed better icephobic properties owing to the formation of multilevel nanostructures by the  $\alpha$ -phase. The icephobic coating using PDMS-PVDF and SiO<sub>2</sub> powder can be applied to large-area surfaces with reliable mechanical properties, and it has considerable potential for applications in coating appliances, such as antennas and objects exposed to harsh environments, including polar regions and the outer space. For the application, a robust, facile, and reliable coating method could be very advantageous.

## ASSOCIATED CONTENT

# **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c22404.

 $\rm SiO_2$  powder size distribution with different milling times, process of preparing an ice sample for the ice adhesion test, ice chamber, schematic of the ice adhesion test, schematic of the peel-off test, XPS spectra of the SS surface, SEM image and EDS analysis of the SiO<sub>2</sub>/ PDMS–PVDF/SS surface according to the PVDF content, FT-IR and XRD analysis of the bare PVDF coating cured at 160 °C and 60% humidity for 3 h on a hot plate, and SEM image of the SiO<sub>2</sub>/PDMS–PVDF/SS surface according to the PVDF content and the SiO<sub>2</sub> powder size (PDF)

Qualitative icephobic comparison between SS and SiO<sub>2</sub>/ PDMS–PVDF/SS (MP4)

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#### Notes

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