Durable Superhydrophobic Coatings for Icephobic Applications

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ABSTRACT

Recent studies about the application of superhydrophobic surfaces for anti-ice properties have found that they can reduce ice adhesion strength significantly compared to bare aluminum surfaces but lack durability. Most superhydrophobic surfaces have micro-nano hierarchical roughness and hydrophobic chemistry. In this work a cost-effective and durable coating was prepared by altering the topography of the surface using silica nanoparticles and fluorinated silanes. The icephobicity of the samples was measured under freezing conditions of -2°C and 32% RH for 20, 40, 60, 80 and 100 minutes. Contact angles of more than 165° and a sliding angle of less than 1° were obtained. The surface morphology and roughness were studied. The durability of the surface was determined using a tape test

INTRODUCTION

Superhydrophobic surfaces have been studied for a variety of applications such as: self-cleaning[1], [2], anticorrosion[3], antipollution[4], oil/water separation[5][6], self-healing[7] and ice repellant[7]–[11] surfaces. Superhydrophobic surfaces have static contact angles above 150^0 and sliding angles below 10^0 allowing easy rolling of water droplets along the surface. Superhydrophobicity can be achieved with surfaces comprising of hydrophobic chemistry (fluorine, alkane, or silicone based moieties) and hierarchical surface topography (both nanometer and micrometer-sized) by mimicking the lotus leaf.

The relationship between water wetting and ice adhesion was studied by Dotan et al. [9] It was found that superhydrophobic surfaces reduce ice adhesion 18 times better than bare aluminum. More recently, Wang et al.[12] showed that ice adhesion strength to superhydrophobic surfaces was ~163.8 times less than that for the bare aluminum samples. Alizadeh et al.[13] demonstrated that ice nucleation under low-humidity conditions can be delayed through control of surface chemistry and texture.

Most superhydrophobic surfaces lose their rough topography under harsh conditions and thus are unsuitable for long term applications. As the stability and durability are important for commercial applications, recent studies have addressed the mechanical robustness under environmental and UV radiation conditions[14], exposure to variety of chemicals[15] and in water environments[16]. Most of the assemblies possess weak bonding and it still remains a challenge to prepare a robust superhydrophobic surface to endure harsh environments. Herein we present a facile and cost effective method to obtain durable superhydrophobic surface by using silica nanoparticles having improved abrasion and outdoor durability.

CHARACTERIZATION

Spin coating (Specialty Coating Systems, Inc, SCS G3 Spin Coater) were used to enable homogenous distribution of the polymer and NPs layers. The contact angle was measured according to the Sessile controlled, contact angle analyzer (Drop Shape Analyzer – DSA100, KRUSS GmbH, Germany). The sliding angle was incorporated into the contact angle analyzer. A drop was deposited on the horizontal substrate and after equilibrium the substrate plane was tilted until the onset of drop motion. The contact angle was measured using a 5 µl water drop. Field-emission Scanning Electron Microscope (FE-SEM) images were taken (Quanta FEG) using 15 kV accelerating voltage and 10 µA emission field. All samples were coated with gold. The roughness was measured using a Dektak XT Profilometer (Bruker Corporation) with a scan length of 750 µm and a scale resolution 0.125 µm. The icephobicity of the samples was measured under freezing conditions of -2^0C and 32% RH for 20, 40, 60, 80 and 100 minutes. Standard Test Methods for Measuring Adhesion by Tape Test – ASTM D3359 was used to evaluate durability. A lattice pattern with either six or eleven cuts in each direction was made in the film, then pressure-sensitive tape was applied over the lattice and then removed.

EXPERIMENTAL

Curing

Four sets of curing were used to find the suitable curing conditions for superhydrophobic surfaces. They are summarized in Table 1. All samples were kept at room temperature before characterization.

Table 1: Curing conditions

Set No.	Curing Condition
1	60 min vacuum
2	60 min vacuum + heat
3	heat
4	Room temperature curing

RESULTS AND DISCUSSION

Contact angle measurements for all four sets are illustrated in Table 2. As can be seen, all samples that were subjected to cure under vacuum and RT exhibited hydrophilic contact angles (CA<90) and high sliding angles (SA>90). However, 60 min curing in vacuum and heat increased dramatically the CA and hydrophobic surfaces were obtained (CA>90 and SA<10). The best results (CA>150 and SA=0) were obtained for heat curing under atmospheric humidity and are shown in Figure 1.

Table 2: Contact angle and sliding angle measurements.

Set No.	Contact angle	Sliding angle
1	70^0-75^0	$>90^0$
2	145^0-150^0	50^0
3	$>150^0$	0^0
4	70^0-75^0	$>90^0$

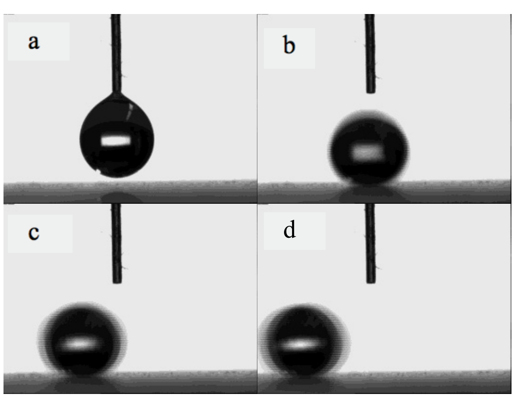

Figure 1: Water drop sliding on superhydrophobic surface (set 3). Horizontal plane.

The surface profile of the superhydrophobic coating was measured using a stylus that is moved over the sample. As it traces across the surface, the movement up and down is recorded as height. The calculated average roughness value was 775 nm indicating sub-micron roughness similar to the lotus leaf[17]. These results explain the high contact angle results and the reduced adhesion of water drops on the surface. This promotes easy sliding across the surface.

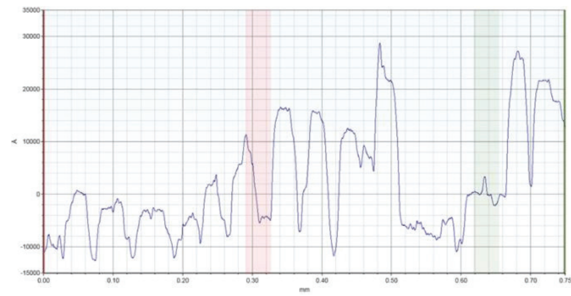

Figure 2: Superhydrophobic surface profile.

The surface morphology and topography were studied using SEM and AFM and are illustrated in Figure 3. As can be seen, a high surface roughness was obtained and silica NPs were completely covering the surface.

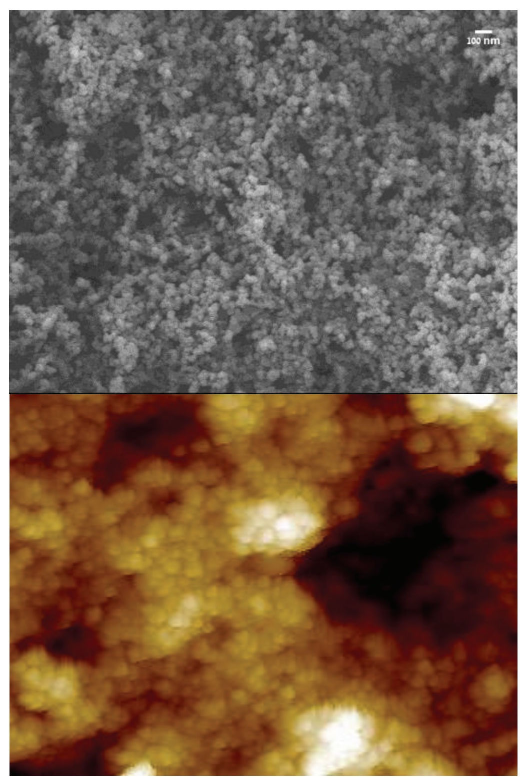

Figure 3: a. SEM image (100 nm scale bar) b. AFM image of superhydrophobic surface.

The superhydrophobic characteristics of the coating under cold and humid environment were studied. The coated substrate was kept outside under freezing conditions of -2^0C and 32% RH for 20, 40, 60, 80 and 100 minutes. Water drops were placed on the surface and slid off easily without tilt (recorded by video). Last, the mechanical stability of the coating was evaluated by a tape test to establish if the level of adhesion of a coating to a substrate is adequate. No visual changes in the coating were observed after rubbing (Figure 4). In addition, the CA and SA measurements showed no change and water droplets still slid easily off the surface. In order to confirm these results, the roughness was measured again after rubbing and is shown in Figure 5. The calculated average roughness value was 767 nm indicating the superhydrophobic coating remained stable even after being rubbed.

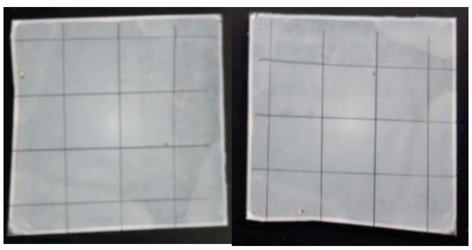

Figure 4: Superhydrophobic surface left-before and right-after tape test

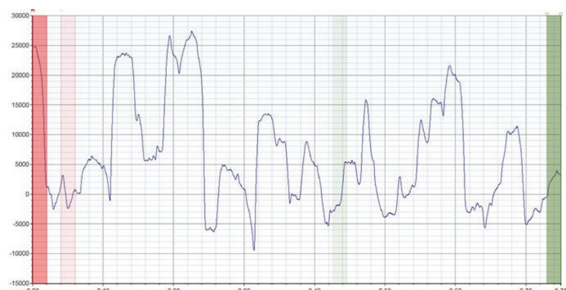

Figure 5: Superhydrophobic surface profile after tape test.

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CONCLUSIONS

A facile and cost effective method to prepare durable superhydrophobic surfaces was presented. Contact angles above 150^0 and 0^0 tilt were obtained under heat curing. The environmental and mechanical durability of the surface were studied. Exposure for 100 min at -2^0C and 32% RH revealed that the surface remained superhydrophobic. The surface also retained its superhydrophobicity after the tape test. Contact angle and roughness measurements were taken before and after the test to confirm these results. These results permit the utilization of superhydrophobic surfaces in practical applications that require high durability.

REFERENCES

[1] P. F. Rios, H. Dodiuk, S. Kenig, S. Mccarthy, and A. Dotan, “Durable ultra-hydrophobic surfaces for self-cleaning applications,” no. September, pp. 1684–1691, 2008.

[2] Y. Chen, S. Chen, F. Yu, W. Sun, H. Zhu, and Y. Yin, “Fabrication and anti-corrosion property of superhydrophobic hybrid film on copper surface and its formation mechanism,” *Surf. Interface Anal.*, vol. 41, no. 11, pp. 872–877, Nov. 2009.

[3] J. Cheng, Z. R. Yang, J. Hai, and J. X. Yang, “Preparation and Performance of RTV Coating for Anti-Pollution Flashover with Superhydrophobicity by Filling CaCO3/SiO2 Composite Particles into Silicone Rubber,” *Adv. Mater. Res.*, vol. 328–330, pp. 1263–1267, Oct. 2011.

[4] H. O. Seo, K.-D. Kim, M.-G. Jeong, Y. D. Kim, K. H. Choi, E. M. Hong, K. H. Lee, and D. C. Lim, “Superhydrophobic carbon fiber surfaces prepared by growth of carbon nanostructures and polydimethylsiloxane coating,” *Macromol. Res.*, vol. 20, no. 2, pp. 216–219, Dec. 2011.

[5] Z. Wang, Q. Li, Z. She, F. Chen, and L. Li, “Low-cost and large-scale fabrication method for an environmentally-friendly superhydrophobic coating on magnesium alloy,” *J. Mater. Chem.*, vol. 22, no. 9, pp. 4097–4105, 2012.

[6] T. Dikić, W. Ming, R. a T. M. van Benthem, a C. C. Esteves, and G. de With, “Self-replenishing surfaces.,” *Adv. Mater.*, vol. 24, no. 27, pp. 3701–4, Jul. 2012.

[7] A. Alizadeh, M. Yamada, R. Li, W. Shang, S. Otta, S. Zhong, L. Ge, A. Dhinojwala, K. R. Conway, V. Bahadur, A. J. Vinciquerra, B. Stephens, and M. L. Blohm, “Dynamics of ice nucleation on water repellent surfaces.,” *Langmuir*, vol. 28, no. 6, pp. 3180–6, Feb. 2012.

[8] S. a Kulinich, S. Farhadi, K. Nose, and X. W. Du, “Superhydrophobic surfaces: are they really ice-repellent?,” *Langmuir*, vol. 27, no. 1, pp. 25–9, Jan. 2011.

[9] S. Dotan, A. Dodiuk, H. Laforte, C. Kenig, “The Relationship between Water Wetting and Ice Adhesion,” *J. Adhes. Sci. Technol.*, pp. 1907–1915, 2009.

[10] S. Farhadi, M. Farzaneh, and S. a. Kulinich, “Anti-icing performance of superhydrophobic surfaces,” *Appl. Surf. Sci.*, vol. 257, no. 14, pp. 6264–6269, May 2011.

[11] L. U. Du, Q. À. Chicoutimi, C. E. Partielle, D. E. L. A. Maîtrise, and E. N. Ingénierie, “Water and ice-repellent properties of nanocomposite coatings based on silicone rubber Propriétés hydrophobes et glaciophobes de revêtements nanocomposites à base de silicone,” no. December, 2010.

[12] C. L. and uzhen Fochi Wang, Fangcheng Lv, Yunpeng Liu, “Ice adhesion on different microstructure superhydrophobic aluminum surfaces,” *J. Adhes. Sci. Technol.*, vol. 27:1, pp. 58–67, 2013.

[13] A. Alizadeh, M. Yamada, R. Li, W. Shang, S. Otta, S. Zhong, L. Ge, A. Dhinojwala, K. R. Conway, V. Bahadur, a J. Vinciquerra, B. Stephens, and M. L. Blohm, “Dynamics of ice nucleation on water repellent surfaces.,” *Langmuir*, vol. 28, no. 6, pp. 3180–6, Feb. 2012.

[14] Y. Xiu, D. W. Hess, and C. P. Wong, “UV and thermally stable superhydrophobic coatings from sol-gel processing.,” *J. Colloid Interface Sci.*, vol. 326, no. 2, pp. 465–70, Oct. 2008.

[15] J. Zimmermann, M. Rabe, G. R. J. Artus, and S. Seeger, “Patterned superfunctional surfaces based on a silicone nanofilament coating,” *Soft Matter*, vol. 4, no. 3, p. 450, 2008.

[16] L. Zhai, M. C. Berg, F. C. Cebeci, Y. Kim, J. M. Milwid, M. F. Rubner, and R. E. Cohen, “Patterned superhydrophobic surfaces: toward a synthetic mimic of the Namib Desert beetle.,” *Nano Lett.*, vol. 6, no. 6, pp. 1213–7, Jun. 2006.

[17] B. Institut, B. Garten, and M. Allee, “Characterization and Distribution of Water-repellent , Self-cleaning Plant Surfaces,” pp. 667–677, 1997.