

Fabrication of Superhydrophobic Coatings Based on Nanoparticles and Fluoropolyurethane

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ABSTRACT: Hydrophobic nanosilica or nanofluoric particles were mixed with fluoropolyurethane resin to fabricate superhydrophobic coatings that have contact angles higher than 145°. These coatings were prepared from the simple mixing of nanoparticles in fluoropolymer and were cured at room temperature. Different fractions of nanosilica, nanofluoric particles, and the combination of them were used to find the best formulations of superhydrophobic coatings. Contact angle, contact angle hysteresis, sliding angle, hardness, and UV durability tests were conducted to find the effectiveness of these coatings. The results showed that only fluoropolyurethane coatings containing nanosilica or the combination of it and fluoric particles were superhydrophobic. Also, the hardness of coatings was increased by raising nanoparticle concentrations. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4136–4140, 2013

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INTRODUCTION

There are many superhydrophobic and self-cleaning surfaces in nature. Some examples are butterfly wings and the leaves of *Nelumbo nucifera* Gaertn (Indian cress). The best well-known example of a self-cleaning surface is the lotus leaf.^{1,2} The scanning electron microscopy (SEM) picture of the surface of lotus leaf shows jutting nubs about 20–40 μm apart each that are covered by a smaller scale rough surface of epicuticular wax.³ The combination of micrometer and nanometer-scale roughness, along with a low surface energy material leads to contact angle higher than 150° and low sliding angle. This effect causes the self-cleaning property to occur. Water droplets on these surfaces can pick up dirt particles and remove contaminants.⁴

When a droplet rests on a solid (flat) surface and is surrounded by a gas, the contact angle (θ) is formed. The apparent contact angles of superhydrophobic surfaces are determined by Wenzel and Cassie–Baxter model.⁵ The θ will be changed to θ^* (apparent contact angle) in the Wenzel state when the liquid fills the voids below the liquid and thus occupies more surface area. There is a relation between apparent contact angle and roughness (r) in his model as in the following equation:

$$\cos \theta^* = r \cos \theta$$

The contact angle of surface will rise when the roughness increases because the droplet in Wenzel state is in intimate

contact with the solid asperities.⁵ Conversely, θ will change to θ^* as in the equation below in the Cassie–Baxter state:

$$\cos \theta^* = \phi(\cos \theta + 1) - 1$$

where ϕ is the area fraction of the solid that touches the liquid. In this state, the droplet rests on the top of solid asperities and the gas is left in the voids below the droplet. The interface area in this model is less than that of a droplet of the same volume on a flat surface or a rough surface in a Wenzel model. Liquid in Cassie state is more mobile and shows less contact angle hysteresis (CAH) than Wenzel state.⁶

Superhydrophobic surfaces can be used in a variety of applications such as the promotion of self-cleaning processes induced by rain water on outdoor surfaces (antennas, traffic lights, etc), the inhibition of clotting in artificial blood vessels, the production of waterproof clothes, and the preservation of monuments.^{5,6} The significant self-cleaning properties of natural superhydrophobic surfaces have inspired many researchers to fabricate superhydrophobic coatings using different methods that mimic the self-cleaning ability. For example, Daoud et al. used sol–gel method to prepare modified hydrophobic silica nanocomposite coating with contact angles higher than 141°. Wang et al. prepared superhydrophobic coatings with nanosized calcium carbonate, polyacrylate, and fluoroalkylsilane.⁸ Hsieh et al. used titanium oxide nanoparticles and perfluoroalkylmethacrylic copolymer to make self-cleaning surfaces.⁹ Seyedmehdi

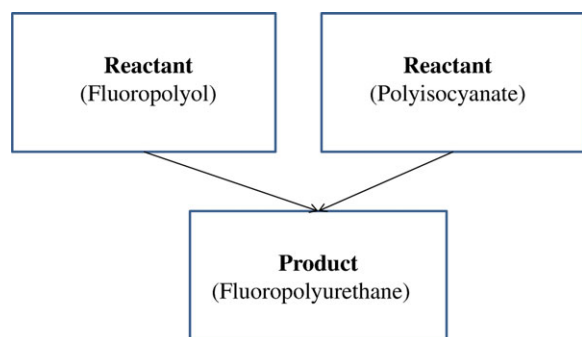


Figure 1. Flowchart of reactants and final product. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

et al. used silicone rubber and nanofluoric particles to fabricate superhydrophobic coatings for high voltage insulators.¹⁰

Most of the superhydrophobic coatings in the literatures are cured in ovens and they are difficult to apply on site due to the high temperature requirement. Furthermore, some of the techniques needed are complicated and with expensive processes.¹¹ Therefore, it is required to make room temperature curing superhydrophobic coatings that are made using a simple and economical process. This study indicates the fabrication of superhydrophobic fluoropolyurethane coatings with nanoparticles that can be cured at room temperature and have contact angles higher than 145°. Furthermore, the effect of nanoparticle combinations on the properties of superhydrophobic coatings is examined.

The hydrophobic properties, hardness, and water/UV durability of superhydrophobic coatings with hydrophobic nanoparticles or their combinations were evaluated in order to find the optimum formulations.

EXPERIMENTAL

Materials and Method

Fluoropolyurethane superhydrophobic coatings (Figure 1) were made from mixing of Fluoropolyol resin (Lumiflon Company, Japan) with nanoparticles and solvent. The nanoparticles were hydrophobic nanosilica, hydrophobic nanofluoric particles, or the combination of them. The final mixture was added to a polyisocyanate resin (Bayer Company, Pittsburgh, Pennsylvania, USA) that acted as the hardener of coating. The basic characteristics of nanoparticles, fluoropolyol, and polyisocyanate are indicated in Tables I and II.

When only one type of nanoparticles was used, the concentrations of nanosilica or fluoric particles were varied between 10 and 40 wt % (dry fraction), whereas when two types of nanoparticles were used together, the total fractions of nanoparticles in the formulations B1–B6 were changed as shown in Table III.

Table I. The Material Characterization of Nanoparticles

	Nanosilica	Nanofluoric particles
Particle size (Average)	20 nm	0.2 μm
Surface area (m ² /g)	100 ± 20	30–50

Table II. The Material Characterization of Polymers

	Fluoropolyol	Polyisocyanate
Density (g/cm ³)	1.06	1.16
OH content (mg KOH/g)	100	-
NCO (%)	-	16.5
Solid percent (wt %)	66	75

The highest combination of aforementioned nanoparticles was 40 wt % and over this point the dispersion of them in coating was not possible.

A new method for mixing of nanoparticles and resin was used to get better dispersion of nanoparticles in coatings. First, nanoparticles were dispersed in the solvent, and then the dispersion was added to the mixture of fluoropolyol and solvent that had been homogenized in a lab scale wet ball mill (Gardco Company, Pompano Beach, Florida, USA) where the final mixture was blended. Aromatic solvents could not be used, because they can affect the hydrophobicity of nanoparticles, so methyl ethyl ketone and mineral spirit were used in this study. The final dispersion and hardener were homogeneously mixed together by a stirrer (the ratio of polyol to hardener was 3 : 1). Higher concentrations of nanoparticles could be blended in this new method compared with the usual way that all coating components were mixed together at one time. Superhydrophobic fluoropolyurethane coatings could be applied on the metallic and glass substrates using common methods like spraying, brushing, and dipping. The samples were cured at room temperature and the hydrophobicity and mechanical property tests were done next day. The thickness of coating was fixed between 50 ± 5 μm.

Characterization

Contact angle, CAH, and sliding angle were used to assess the hydrophobicity of coatings.^{12,13} Contact angle and CAH were measured by the sessile drop method. Surface heterogeneity is evaluated by CAH and it is the difference between advancing and receding contact angles. When a pipette injects a liquid onto a solid, the liquid will form a contact angle with the solid surface. When increasing the amount of liquid by pipette, the volume of droplet and its contact angle will increase, but its boundary will remain constant until it suddenly advances outward. The contact angle of the droplet immediately before advancing outward is named advancing contact angle.¹² The

Table III. The Nanosilica and Nanofluoric Particle Fractions in Formulations (from B1 to B6) Containing Nanoparticles Combination

Total nanoparticles (wt %)	Nanosilica (wt %)	Nanofluoric (wt %)
20 (B1)	10	10
30 (B2)	20	10
40 (B3)	30	10
30 (B4)	10	20
40 (B5)	20	20
40 (B6)	10	30

receding contact angle is measured when the liquid is pumped away from the droplet. In this case, the volume and contact angle of droplet will reduce, but its boundary will remain constant until it suddenly recedes inward.¹³

Contact angle, advancing angle, and receding angle were measured by using Rame-Hart 100 Goniometer (Rame-Hart Instrument Company, Succasunna, New Jersey, USA) in this work. Sliding angle also showed the heterogeneity of surface and was measured by injecting a droplet on a surface and tilting the surface to find the angle of the surface to the horizontal plain when the droplet starts to slide.¹⁴ The contact and sliding angles of five different points on the coatings were measured (25°C) and their averages were reported. The error range for each contact angle was $\pm 5^\circ$ while the error range for each sliding angle was $\pm 0.5^\circ$. Also, CAH was measured only for coatings that had contact angles equal or higher than 140° .

A scanning electron microscopy (SEM), Hitachi S-2600 (Hitachi, Pleasanton, CA), was utilized to verify the micro and/or nanostructure of superhydrophobic coatings. All samples were gold-sputtered before scanning.

Weathering tests and UV durability of superhydrophobic coatings were done by Q-Sun Xenon Test Chamber (Q-Lab Company, Westlake, Ohio, USA). Following ASTM G155, this practice used xenon arc light and water apparatus to reproduce the

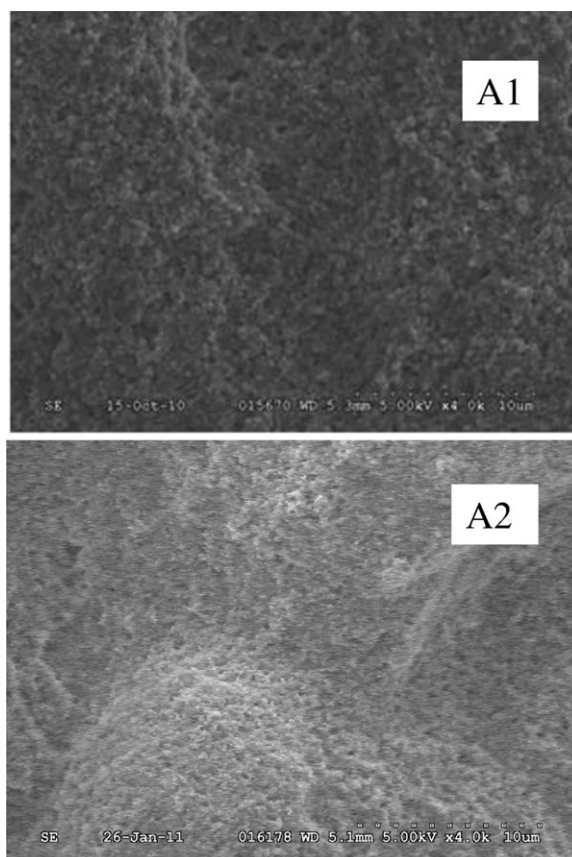


Figure 2. SEM pictures of superhydrophobic coatings with 40 wt % nanosilica (A1) and the combination of 20 wt % nanosilica and 20 wt % fluoric particles (A2).

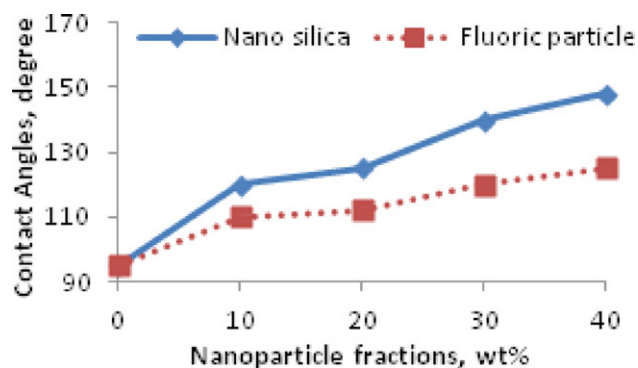


Figure 3. Contact angles of coatings with two different nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weathering effects that happened when coatings are exposed to sunlight and moisture in actual use.¹⁵ Samples coated with the superhydrophobic coatings were exposed to UV light and water spray for 1000 h. The contact angles of samples were measured every 200 h to check the changes in hydrophobicity of coatings.

Pencil test¹⁶ was used to measure the hardness of coatings. A set of calibrated wood pencils with different scale of hardness was used wherein the softest is 6B and the hardest is 6H.

RESULTS AND DISCUSSION

Morphology Structure of Coatings

Figure 2 displays the results of SEM pictures of flouropolyurethane superhydrophobic coatings with nanosilica and the combination of nanosilica and nanofluoric particles, respectively (the scale of SEM picture is $10 \mu\text{m}$). The pictures of other superhydrophobic coatings were similar to these pictures and are not shown here. The surface of superhydrophobic coatings had micro textures that are one of the important factors for being superhydrophobic.

The combination of nano- and microstructure together with low surface energy ensures the low wettability. The interface area between water droplet and surface is reduced by air pockets that are formed when the air is trapped in the textures. Therefore, the water droplet cannot spread on the superhydrophobic surfaces.¹⁷

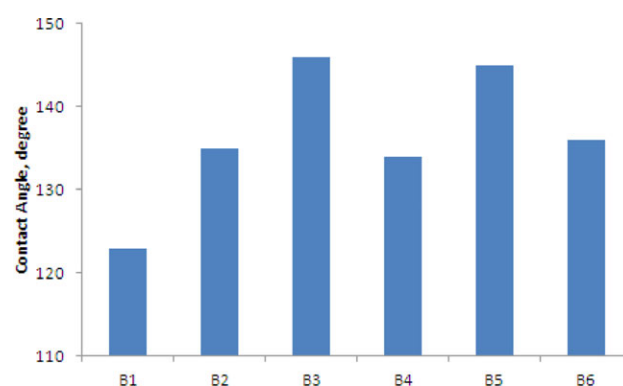


Figure 4. Contact angles of coatings with the combination of nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Contact Angle Hysteresis of Superhydrophobic Coatings

	CAH	Contact angle
40% S	5°	148°
30% S	12°	140°
20%S+20%F	6°	145°
10%S+30%F	5°	146°

S: nanosilica, F: fluoric particles.

Hydrophobic Properties of Coatings

Figure 3 presents the variation of contact angle of coatings as a function of nanoparticle fractions. The contact angles increased with rising nanoparticle fractions and the highest contact angle was achieved at point containing 40 wt % nanosilica.

Also, the results of fluoropolyurethane coatings with the combination of nanosilica (S) and nanofluoric particles (F) shows that the contact angles would increase with increasing nanoparticle concentrations (Figure 4). The best result was achieved at point containing 30 wt % nanosilica and 10 wt % nanofluoric particles (formulation B3). The roughness of coatings will rise by increasing the nanoparticles fraction and this fact can increase the contact angle of final coatings according to Wenzel or Cassie–Baxter theory.¹⁸

The CAH of superhydrophobic coatings with contact angles equal or higher than 140° was summarized in Table IV. It can be found from the results that coatings with contact angles less than 145° did not present CAH less than 10° and the water droplet on these surfaces cannot slide well. Generally, the water droplet on the surfaces with CAH less than 7° is mobile and follows Cassie–Baxter’s state,¹⁹ so the coatings containing 30 wt % nanosilica follows Wenzel’s state and may not show good water durability.

Figure 5 displays the changes of sliding angles of fluoropolyurethane coatings with nanoparticle fractions. The results demonstrated that the sliding angles would reduce by increasing nanoparticle fractions. However, only fluoropolyurethane

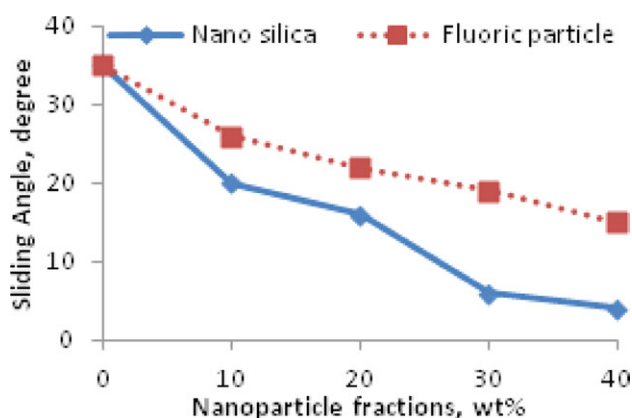


Figure 5. Sliding angles measured for coatings with two different nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

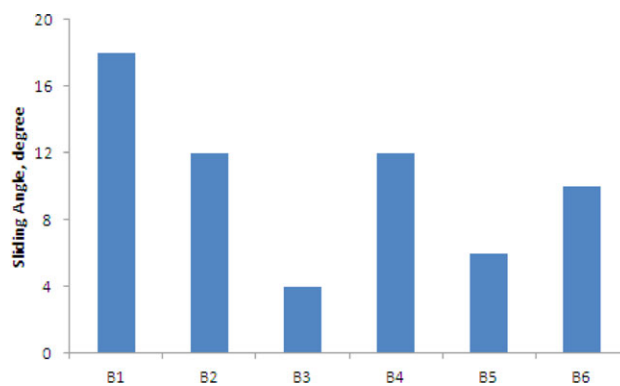


Figure 6. The sliding angle changes of coatings with the combination of nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coating with 40 wt % nanosilica showed sliding angles less than 5°.

The results of fluoropolyurethane coatings with the combination of nanosilica (S) and nanofluoric particles (F) also illustrate that the sliding angles would decrease with increasing nanoparticle concentrations (Figure 6). The best result was attained at 30 wt % nanosilica and 10 wt % nanofluoric particles (formulation B3).

Finally, it can be observed from the results of hydrophobicity tests that only nanosilica could provide superhydrophobic properties in coatings and fluoric particles can make superhydrophobic coatings only in combination with nanosilica. This property of nanosilica may be related to its particle size that is less than fluoric particles and can build rougher surfaces. Furthermore, the type of polymer may influence the fabrication of superhydrophobic coatings because both nanoparticles in this experiment were hydrophobic while only nanosilica could make contact angles higher than 140°.

Weathering Durability and Hardness of Coatings

The contact angles of fluoropolyurethane coatings versus UV exposure time are displayed in Figure 7. This test was done on substrates that were coated by superhydrophobic coatings that had contact angles equal or higher than 140°. The coatings with 30 wt % nanosilica that had CAH equal to 12° could not pass

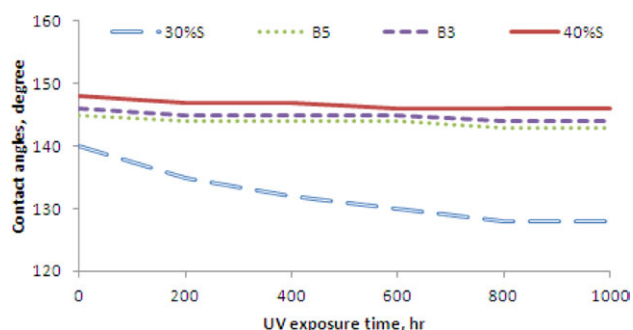


Figure 7. Contact angles against UV exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. The Hardness of Fluoropolyurethane Coatings Versus Nanoparticle Fractions

(Wt %)	Hardness (F)	Hardness (S)
0	H	H
10	H	H
20	H	2H
30	2H	3H
40	2H	3H

this test while other formulations exhibited good UV and water durability.

As stated in Table IV, the superhydrophobic coatings with CAH higher (Wenzel's state) than 7° cannot repel water from the surface, so the water durability of coating with 30 wt % nanosilica reduced during water and UV durability test. The water in the Wenzel's state fills the void in the surface while in the Cassie–Baxter's state, the water sits on the air pocket. Therefore, water cannot move well on the surface in the first state and the coatings did not indicate remarkable durability.^{20,21}

It can be realized from the results of this test that the base materials which were fluoropolyurethane, nanosilica, and nanofluoric particles employed in the superhydrophobic coatings have strong weather resistance and coatings with contact angles higher than 145° can be used for outdoor applications.

As it can be seen in Table V, the hardness of fluoropolyurethane coatings rises with increasing the nanoparticle fractions (S: nanosilica or F: nanofluoric particles). The highest hardness was related to coatings with nanosilica at 40 wt %. It is clear that nanosilica could make more robust films.

Also, Table VI indicates that the hardness of fluoropolyurethane coatings with the combination of nanoparticles increased with rising nanomaterial fractions. The highest hardness was achieved at 30 wt % nanosilica and 10 wt % fluoroc particles (formulation B3).

Generally, the hardness of fluoropolyurethane coatings was increased with the nanoparticle concentrations as well as contact angles, so superhydrophobic coatings can also be used for applications that need scratch resistance too.

CONCLUSION

A method was used to fabricate fluoropolyurethane superhydrophobic coatings that were cured at room temperature. The effects of two different nanoparticles including nanosilica, nanofluoric particles, or the combination of them on contact angles, CAH, sliding angles, hardness, and weathering durability of coatings were examined to find good formulations that can provide high contact angle, low CAH, and sliding angle. The results of these experiments determined that fluoropolyurethane coatings with 40 wt % nanosilica, with the combination of 20 wt % nanosilica and 20 wt % fluoroc particles or the combination of 30 wt % nanosilica and 10 wt % fluoroc particles could pass weathering test and showed CAH less than 10° . Hence, only these formulations could fabricate superhydrophobic coatings that had good durability. Moreover, the hardness of coatings

Table VI. The Hardness of Coatings Containing the Combination of Nanoparticles

Formulations	Hardness
B1	H
B2	2H
B3	3H
B4	H
B5	2H
B6	2H

increased with the rising nanoparticle fractions and the highest hardness was 3H.

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