Development of Excellent Water-Repellent Coatings for Metallic and Ceramic Surfaces

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Abstract— One of the most fascinating properties of various insects and plant surfaces in nature is their water-repellent (superhydrophobicity) capability. The nature offers new insights to learn and replicate the same in designing artificial superhydrophobic structures for a wide range of applications such as micro-fluidics, micro-electronics, textiles, self-cleaning surfaces, anti-corrosion, anti-fingerprint, oil/water separation, etc. In general, artificial superhydrophobic surfaces are synthesized by creating roughness and then treating the surface with low surface energy materials. In this work, various super-hydrophobic coatings on metallic surfaces (aluminum, steel, copper, steel mesh) were synthesized by chemical etching process using different etchants and fatty acid. Also, SiO_2 nano/micro-particles imbedded polyethylene, polystyrene, and poly(methyl methacrylate) superhydrophobic coatings were synthesized on glass substrates. To know the applications of the coatings, surface morphology, contact angle, self-cleaning, anti-icing, anti-fogging, corrosion-resistance, and water-repellent characteristics were investigated at various conditions. Furthermore, durability of coatings was also studied by performing thermal, ultra-violet, and mechanical stability tests. The surface morphology confirms the creation of rough microstructures by chemical etching or by embedding particles and the contact angle measurements reveals the superhydrophobic nature. Experimentally it is found that the coatings have excellent self-cleaning, anti-corrosion, anti-fogging, anti-icing, and water-repellent nature. These coatings also withstand mechanical disturbances such surface bending, adhesive peeling, and abrasion. Coatings are also found to be thermal and ultra-violet stable. Additionally, metallic coatings are also reproducible. Hence aforesaid durable superhydrophobic surfaces have many potential industrial applications.

Keywords- Superhydrophobic; Water-repellent; Anti-corrosion; Self-cleaning

I. INTRODUCTION

Superhydrophobic surfaces are the surfaces with water contact angle greater than 150° and readily repel water. Naturally occurring non-wettable surfaces has inspired scientists to mimic their water repellent [1] and self-cleaning [2] behaviour in preparation of artificial superhydrophobic surfaces. In general, preparation of artificial superhydrophobic surfaces involves two approaches. First approach is to create rough structure on hydrophobic surface and the second approach is to modify the rough surface with materials of low surface energy. Different fabrication techniques to achieve artificial superhydrophobicity are available such as anodic oxidation [3-5], chemical deposition [6], chemical etching [7-11], chemical vapor deposition [12-15], colloidal self-assembly [16-18], electrospinning [19-20], sol–gel [21-22] and some others [23-24].

Some of these are simple and inexpensive; however, some of these involve multistep procedures and harsh conditions or require specialized reagents and equipment, which leads to increase the cost of coating. Since several years, the endless efforts have been carried out to develop the synthesis techniques to prepare super-hydrophobic/oleophobic surfaces for industrial scale which are economical, easy to produce, environmental safe, high efficient, well adhesive, compatible, and high durability; but most of them are restricted to only fundamental research in laboratory and there is still much work required to be done for super-hydrophobic/oleophobic surfaces preparation on commercial scale. In this work, superhydrophobic coatings on metallic and ceramic surfaces were developed by employing dip-coating, phase separation, chemical etching, and immersion techniques.

II. EXPERIMENTAL DETAILS

Superhydrophobicity on metallic surfaces (aluminium, steel, copper, brass) were prepared by immersing them in alkaline (NaOH/KOH) or acidic (HCl, HNO_3, HCl+HNO_3) followed by immersing/dipping in fatty acid (lauric, stearic) or polymer (LLDPE, PS, PMMA) solutions. SiO_2 nano/micro-particles embedded polymer (LLDPE, PS, PMMA) or low surface energy materials (OTS, TMS) superhydrophobic coatings on glass substrates were fabricated using dip-coating technique. Porosity of above polymer coatings was also varied using non-solvent (ethanol) by employing phase separation method. Surface morphologies of the prepared samples were examined with scanning electron microscopy (SEM) (Nova NanoSEM, FEI). Contact angle measurement was done at room temperature through sessile drop method using Drop Shape Analyser (DSA) (25, Kruss, Germany) with droplet of distilled water of 7-10 µL drop volume. Additionally, durability for UV exposure, heat treatment, and mechanical disturbances on superhydrophobic was studied. Further, regeneration of coatings was also done. Along with, self-cleaning, anti-fogging, anti-icing, corrosion-resistant, and water repelling characteristics were also studied.

Durability of the superhydrophobic surface was checked by adhesive tape peeling, abrasion, and surface bending tests. Adhesive tape peeling test was carried out by using commercially purchased insulation tape and multiple times peeling was done on coatings. Abrasion test was carried out by applying a weight of 50 g (0.5 N) wrapped with a microfiber cloth which was moved back and forth direction along the coated surface. Both tests were continued until coatings lost its superhydrophobicity. For surface bending tests, coated samples were simply bent in different directions and angles, and multiple times folding and de-folding bending. Water droplets were placed at different positions on bending areas to check superhydrophobicity.

A simple thermal test was carried out in a hot air oven by varying the temperature from 80 to 270 °C. Coated samples were kept at different temperature for one hour period. After cooling the samples, contact angles were measured to check the superhydrophobicity. UV stability test was carried out by exposing coatings to an ultraviolet light of wavelength 254 nm for 55 hours in a UV curer (UltraV-C1, Apex Instruments Co. Pvt. Ltd, India) and contact angle was measured at regular time interval to check the superhydrophobicity.

Floatation on water surface test was carried out by keeping coated sample on the water surface in a petri dish and floatation time was recorded till sample started sinking. For water jet impact test, water jet which is released from a 25 ml syringe was sprayed on uncoated and coated samples. Water jet was kept about 3 cm above the surface with angle of nearly 45° for 1 minute. The interaction between the water jet and the sample surfaces was observed. For low temperature condensation, uncoated and coated samples were kept in the deep freezer for five hours and then they were kept in humid atmosphere of 80% relative humidity.

The self-cleaning test was carried out by simply sprinkling small amount of graphite powder taken from a pencil led on the uncoated and coated surfaces. Water droplets were slowly dropped on the graphite powder sprinkled surfaces and flow of droplets were recorded.

The corrosion test was carried out by simply immersing the superhydrophobic surface in 5% acetic acid solution and 3% by weight sodium chloride (NaCl) solution. At regular time interval, contact angles were measured to check the superhydrophobicity. For this, superhydrophobic metallic surface was continuous heated at 400 °C for 24 hours such that coating surface was fully damaged.

To regenerate the destroyed superhydrophobic coating, substrate was again immersed in ethanol solution of lauric acid for 30 min and then air dried for 24 hours. After that, contact angle of re-coated surface was measured.

III. RESULTS AND DISCUSSION

Addition of nano/micro-particles and/or generation of porosity in to polymer matrix increase the surface roughness. The same is clearly seen by modification of surface morphologies of LLDPE by adding SiO_2 and/or creating porosity in fig. 1 (a-c). Tailoring the amount of SiO_2 nanoparticles and porosity generates superhydrophobic surfaces with water contact angle more than 150°.

Chemical reactions of base/acid with metal surface result in an etching process leading to a rough microporous structure on the surface. After etching metal substrates, the samples were immersed in fatty acid solution which results in the formation of sponge like layer on the surface as shown in fig 2 (a-c) because the carboxyl in the positive end of the lauric acid reacts with the hydroxyl or the metal atom through dehydrating process. The formation of a rough micro-cratered surface, in combination with a modified surface chemistry arising from lauric acid, contributes to the creation of superhydrophobic and water contact angles for metallic surfaces are found to be more than 150°.

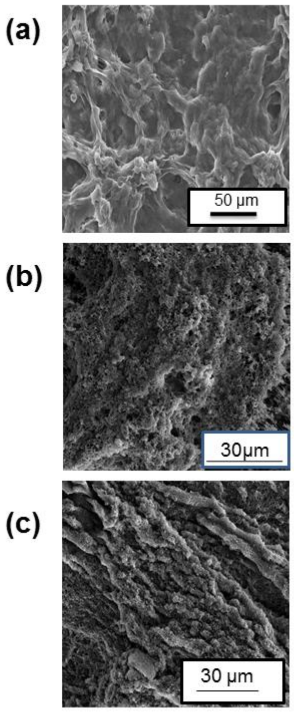

Fig. 1. SEM images of superhydrophobic coating of (a) non-porous LLDPE/SiO$_2$, (b) porous LLDPE, (c) porous LLDPE/SiO$_2$ on glass substrates.

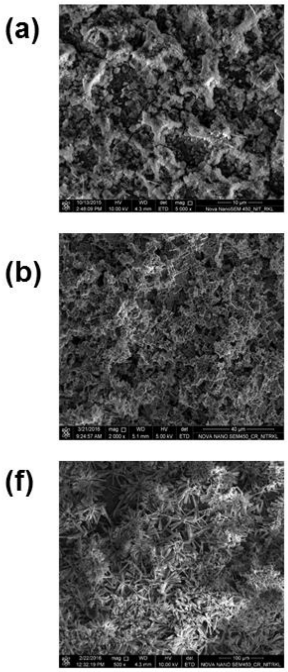

Fig. 2. SEM images of superhydrophobic coatings on (a) aluminium using NaOH etchant, (b) aluminium using HCl etchant, (c) copper using HCl etchant.

For successfully implementation of these superhydrophobic coatings in different applications, self-cleaning, corrosion-resistance, anti-fogging, anti-icing, water-repellent were investigated at various conditions. Furthermore, the stability of these coatings was also evaluated by conducting thermal and mechanical stability tests. Coatings exhibit the excellent self-cleaning behavior (Fig. 3). These coating also show their excellent corrosion-resistant and anti-icing properties.

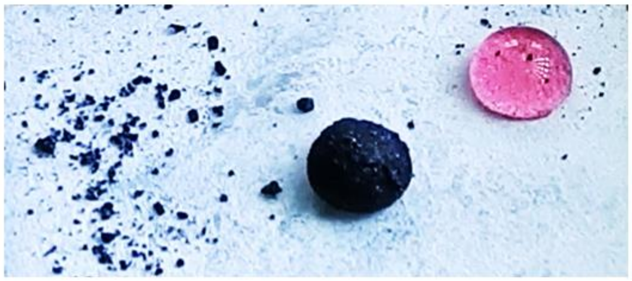

Fig. 3. Optical images of self-cleaning behavior of coating.

All fabricated superhydrophobic coatings exhibited anti-fogging property. For example, Fig. 43 shows the anti-fogging ability of superhydrophobic aluminium surface.

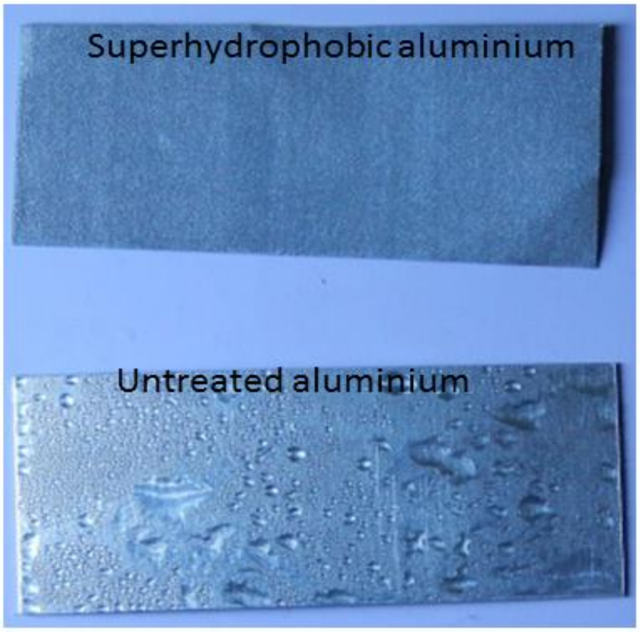

Fig. 4. Optical images of anti-fogging behavior of untreated and superhydrophobic aluminium surface.

In condensation due to low temperature experiment, untreated and superhydrophobic aluminium surfaces were placed in a refrigerator for five hours and later they were placed in open environment. For untreated aluminium surface, water droplets can be seen getting accumulated on the surface as soon as it was kept in the open environment.

While for superhydrophobic aluminium surfaces, few spherical bead shaped water droplets are formed. In both condensation tests, it is observed that the superhydrophobicity lost is restorable after the water droplets completely dried of.

Above superhydrophobic surfaces were also exposed to elevated temperature. Metallic superhydrophobic coatings remain unaffected upto 170 ºC and polymer based coatings are found to be stable upto 120 ºC. Metallic surfaces come in humid conditions or comes in contact of water for longer time, they becomes corrode. The superhydrophobic coatings on metals are unaffected in acidic/base solution for several hours, however polymer based coatings on glass substrates are found to be stable for several weeks. Superhydrophobicity of coatings were teased by exposing UV light and it confirms that coatings are stable in UV light for several days.

For having real practical applications, mechanical durability is essential for superhydrophobic surfaces. If the surface fabricated is too delicate, then it cannot promise long life of superhydrophobicity which is uneconomical. The tests carried out for demonstrating mechanical durability here are adhesive peeling test, abrasion test and bending. Mechanical disturbances due to bending and folding have not much effect on the superhydrophobicity (Fig. 5). This figure shows how the water droplets form bead like shape at 90° bending and the water droplets in kink region which were formed due to 180° bending and water droplets still maintain their shape and roll off easily. Further when superhydrophobic samples are bended several times and water droplets are placed in kink regions, surprisingly water droplets still maintain their shape and roll off easily, i. e. superhydrophobic nature also withstand mechanical disturbances.

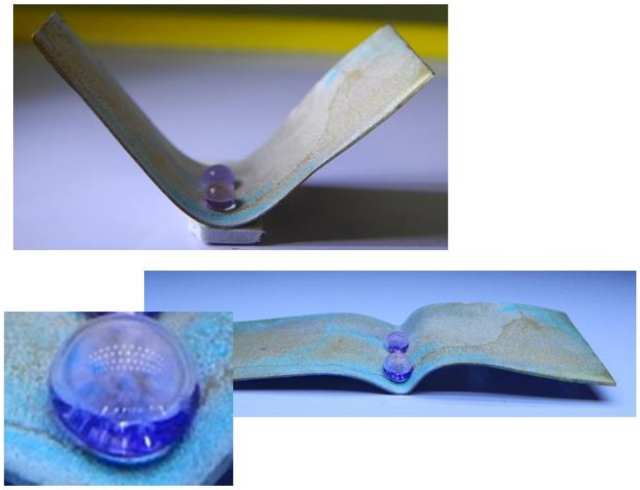

Fig. 5. Optical image of superhydrophobic copper surface bending test.

Coating also sustains several times of adhesive peeling test (Fig. 6).

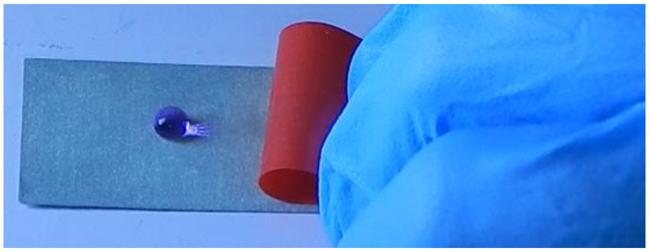

Fig. 6. Optical image of tape peeling test on superhydrophobic steel surface.

The surface regains its superhydrophobic characteristic, confirming that this coating is regenerable. Floating test and water jet impact assert coatings' excellent water repelling nature as shown in fig. 7 and fig. 8. The floating test is carried out by leaving both the uncoated and coated samples to float on the surface of water in a petri-dish. Uncoated sample sinks down immediately in the water whereas coated sample remains floating on the water surface for several weeks (Fig. 7), showing excellent buoyancy nature.

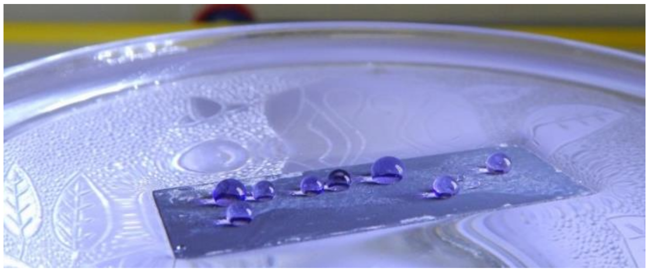

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Fig. 7. Optical image superhydrophobic steel surface floating on water surface.

Water jet impact test is performed on both uncoated and coated metallic or ceramic surfaces. When water jet is sprayed on the surfaces, uncoated surface did not prevent the water from spreading on its surface while, superhydrophobic surface bounces off the water jet in the opposite direction as shown in Fig. 8. This is because of the lowered surface energy and the presence of air pockets on the surface which does not allow the impacting water jet to enter into the rough structure of the surface. This asserts the strength of the superhydrophobic coating. The water jet is targeted at the same position for more than 1 min and the water jet is still continuously bouncing off the surface, indicating excellent mechanical strength of coatings.

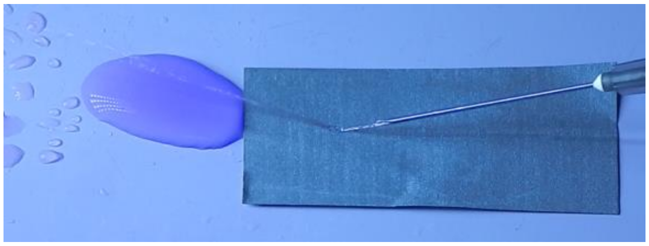

Fig. 8. Optical image of water jet impact test on superhydrophobic aluminium surface.

IV. SUMMARY

In this paper, superhydrophobic coatings on metallic and ceramic surfaces were prepared. To evaluate the coatings' characteristic, wettability, surface morphology, mechanical stability, thermal stability, UV stability, water repellent, self-cleaning, anti-icing, anti-fogging, and corrosion properties were also investigated. It is confirmed the presence of a rough microstructures on the treated surfaces and the contact angle measurements reveal the superhydrophobicity. Water jet impact and water floatation tests show the excellent water repellent nature of coatings. Also thermal, mechanical and UV stabilities of coatings are also evaluated. Further, coating shows the excellent self-cleaning, corrosion-resistant, anti-icing, and anti-fogging properties. Superhydrophobic coatings on metallic surfaces also show reproducible nature. These mechanical, thermal and UV stable and regenerable superhydrophobic coatings with excellent water repellent, anti-corrosion, self-cleaning, anti-fogging, anti-icing properties have great industrial applications.

V. REFERENCES

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AUTHORS' BACKGROUND

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Dr. Aditya Kumar	Assistant Professor	Nanomaterials, Tribology, Function coatings, Materials Science	