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Fabrication of Silica/PMMA Composite Based Superhydrophobic Coating by Drop Casting Method

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The dirt particles are detached and carried away by freely rolling water drops from superhydrophobic surfaces performing self-cleaning ability. Hence, the self-cleaning superhydrophobic surfaces are gaining huge attention of industries due to their useful day-to-day applications. Herein, we synthesized the hydrophobic silica nanoparticles by sol-gel processing of methyltrimethoxysilane (MTMS). The nanocomposite solution consisting suspension of silica nanoparticles in poly(methylmethacrylate) (PMMA) was applied on glass substrate by simple drop casting method. The microscale roughness of the coating facilitated air trapping in the rough protrusions resulting water contact angle higher than 168°. The self-cleaning ability and mechanical durability of the superhydrophobic coating were also evaluated.

Keywords: Superhydrophobic, Self-cleaning, Hydrophobic silica, Lotus effect, Wetting.

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1. INTRODUCTION

On landing, the water drops acquire spherical shape and become restless on the lotus leaves. The air pockets get trapped inside the wax covered rough papillae microstructure of lotus leaf and the water drops simply sit over the composite air/solid interface. Such extremely nonwetting surfaces on which the water drop exhibits contact angle higher than 150 ° are well known as superhydrophobic surfaces [1]. The lotus leaves are unique model of self-cleaning surfaces in the nature, which inspires to design artificial superhydrophobic surfaces. Since last two decades, number of reports on the fabrication of superhydrophobic surfaces are available due to its essential application in various fields, such as self-cleaning [2], anti-adhesive [3], anti-icing [4], anti-bacterial [5], oil-water separation [6] and so on [7, 8]. Generally, the superhydrophobic surfaces can be fabricated by either creating micro/nanoscale roughness from low surface energy materials or depositing a layer of low surface energy materials on rough solid surfaces [9]. Wenzel and Cassie-Baxter's models explained the importance of roughness on the wettability of the solid surfaces [10].

Abundant reports on the use of poly(methylmethacrylate) (PMMA) in combination with different nanoparticles to attain superhydrophobic surfaces are available [11-18]. Manoudis et al. [11] have simply sprayed the suspension of hydrophilic silica nanoparticles and PMMA on glass substrate and found that the static contact angle increased rapidly with concentration of silica nanoparticles and reached maximum value 154°. Sriboonruang et al. [12] prepared transparent superhydrophobic nanocoating by adding fumed silica nanoparticles in polystyrene and PMMA solution. After annealing the coatings at temperatures higher than 200 ºC, the wetting properties were transferred to superhydrophilic due to the decay of the polymer into hydrophilic monomers. Wang et al. [13] have studied the effect of amount of silica nanoparticle concentration in PMMA solution to attain superhydrophobic nanocomposite films. The wetting properties of pristine PMMA was improved to superhydrophobic by introducing high dosage of silica nanoparticles in PMMA solution. On the contrary, Latthe et al. [14] achieved semi-transparent and self-cleaning superhydrophobic coatings from the nanocomposite of silica-PMMA. The low loading of PMMA could effectively improve the mechanical durability as well as the optical transparency of the superhydrophobic coating.

Pan et al. [15] have spray coated the mixture of PMMA and silica nanoparticles on steel surface which revealed water contact angle ~ 150° and sliding angle ~ 2°. In the other report [16], the dip-coated PMMA/SiO_2 film exhibited water contact angle of 160° and transmittance of 95 %, while spray coated film exhibited water contact angle 140° and 85 % of transparency. These durable and optically transparent superhydrophobic films exhibited an excellent self-cleaning property. Yoon et al. [17] have prepared a self-cleaning, transparent, superhydrophobic coating by electrospraying a suspension of alumina nanoparticles in the mixture of MTMS and PMMA on ITO substrate. Liu et al. [18] have developed translucent superhydrophobic surface by spraying hybrids of PDMS and PMMA prepared in THF solution. The obtained superhydrophobic film strongly repelled water and various organic liquids and revealed stability against corrosive liquids, sandpaper abrasion tests, and

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water droplet impact tests. In the present research work, a dispersion of silica nanoparticle in PMMA was applied on glass substrate by drop casting method. The wettability of the coating was strictly dependent on amount of silica nanoparticles in PMMA structure.

2. EXPERIMENTAL

2.1 Materials

Methyltrimethoxysilane (MTMS, 98 %), Poly(methylmethacrylate) (PMMA, Mw ~ 120,000), N, N-Dimethylformamide (DMF, ≥ 99.9 %) were purchased from Sigma Aldrich, USA. Ethanol (99.9 %) and ammonia solution (28 %) were obtained from Sisco Research Laboratories Pvt. Ltd., India. Microslide glasses were obtained from BLUE STAR, India.

2.2 Synthesis of Hydrophobic Silica Nanoparticles

Hydrophobic silica nanoparticles were obtained by the following procedure: 5 ml double distilled water and 2 ml ammonia were mixed in 40 ml ethanol and kept for stirring for 10 h. A 6 ml MTMS was slowly added in above solution and stirred overnight to form a gel. A gel was dried at 80 ºC for 12 h. The dried gel was cut into small pieces and kept for annealing at 150 °C for 6 h. The obtained powder was grinded well using mortar and pestle to achieve fine silica nanoparticles. Due to non-hydrolysable methyl group in MTMS, the obtained silica nanoparticles are hydrophobic in nature.

2.3 Preparation of Superhydrophobic Surface

The preparation of silica/PMMA composite superhydrophobic coating on glass substrate was schematically illustrated in Fig. 1. At first, a 20 mg/ml PMMA was prepared in DMF. The obtained hydrophobic silica nanoparticles were dispersed in PMMA solution by overnight stirring at ~ 50 °C. The coating solutions with different concentrations of hydrophobic silica nanoparticles in PMMA solution (25, 50, 75 and 100 mg/ml) were prepared and labeled as SP-1, SP-2, SP-3 and SP-4, respectively. The coating solution was deposited on clean glass substrate (40 mm × 25 mm) by drop casting method. A 250 µl of silica/PMMA solution was dropped on the horizontally placed glass substrate, which covered all the substrate area uniformly. This coating was dried at 150 °C for 4 h at a ramping rate of 1 °C per 5 min.

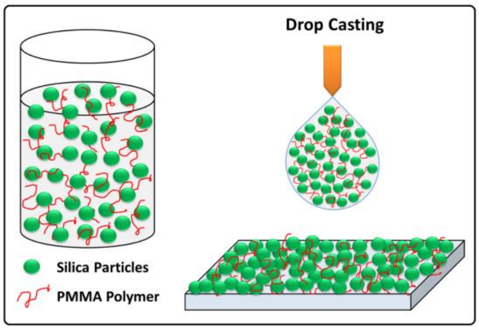

Fig. 1 – Schematic diagram illustrating the preparation of a silica/PMMA composite coating on glass substrate by drop casting method

2.4 Characterizations

The surface morphology, surface roughness, surface chemistry and surface wetting properties of the drop casted superhydrophobic coatings were investigated using Field Emission Scanning Electron Microscopy (JEOL, JSM-7610F, Japan), laser microscope (KEYENCE, VK-X200 series), Fourier transform infrared spectroscopy (FT-IR, JASCO, FT/IR-6100), and Contact angle meter (HO-IAD-CAM-01, Holmarch Opto-Mechatronics Pvt. Ltd. India), respectively. The photographs of water drops on superhydrophobic surface were captured using camera. The averaged values of water contact angles (WCA) measured at several positions on the sample are reported.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology, Roughness and Chemical Properties of the Coatings

The surface morphology plays important role in wettability of the solid surface. Especially, the rough micro/nanoscale surface morphology is desirable to attain extremely non-wettable superhydrophobic surfaces. The silica nanoparticles were incorporated in the PMMA structure to enhance the roughness of the coating. Fig. 2 depicts the FE-SEM (Fig. 2a, b) and laser microscope (Fig. 2c, d) images of SP-1 and SP-3 samples, respectively. The SP-1 sample revealed smooth surface morphology constituting the aggregated silica nanoparticles embeded inside the PMMA structure. The smooth morphology of the coating appeared due to the excess of PMMA in the coating material. This coating showed average roughness of nearly 5.13 µm (Fig. 2b). The possibility of air trapping might be very less in this microstructure and hence the surface roughness can be enhanced by increasing the concentration of silica nanoparticles in the coating solution. The SP-2 samples exhibited relatively rough morphology with the surface roughness of nearly 10.54 µm. As shown in Fig. 2c, the SP-3 sample depicts rough microstructure with optimum combination of silica nanoparticles in PMMA. The increased silica nanoparticle content in PMMA effectively enhanced the surface roughness to 18.36 µm. Due to this high surface roughness, the chances of air trapping in the rough structure increases. The air filled rough surface effectively reduces the adhesion between water and coating surface. The increase in surface roughness can be attributed to the switching of Wenzel wetting state into the Cassie-Baxter wetting state. The surface morphology of the SP-3 sample resembles with the earlier report [19] on silica-PMMA nanocomposite coating. However, the surface morphology of SP-4 sample revealed loosely connected aggregated grains of silica-PMMA nanocomposite with micrometer scale voids in between the surface structure.

The FT-IR spectra of drop casted silica/PMMA composite (SP-3 sample) is shown in Fig. 3. The characteristic absorption peaks were recorded in the range of 450-4000 cm^{-1}. The absorption peaks characteristic of silica like stretching vibration at 1080 cm^{-1} and peak at 800 cm^{-1} are observed in the spectrum [19]. The peaks observed at 2950 and 1400 cm^{-1} are due to stretching and bending modes of C–H bond and the peaks observed at 765 and 1265 cm^{-1} are due to the Si–C bonds [20].

These peaks correspond to the presence of methyl groups that enhances the hydrophobic properties of the coating. The peak at around 1600 cm^{-1} and the broad absorption band at around 3400 cm^{-1} were observed due to the –OH groups [21]. The presence of –OH groups arises due to the hydrolyzed methoxy group of MTMS during sol-gel process.

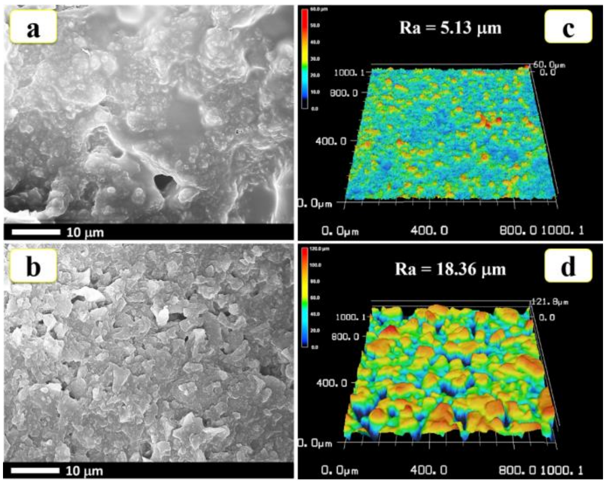

Fig. 2 – FE-SEM (a, b) and laser microscope (c, d) images of SP-1 and SP-3 samples, respectively

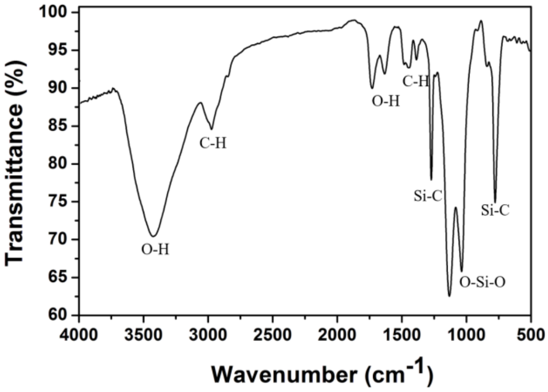

Fig. 3 – FT-IR spectra of SP-3 sample

3.2 Wetting and Self-cleaning Properties of the Coatings

The drop casted coatings exhibited change in surface morphology and surface roughness with increasing loading of silica nanoparticles in PMMA structure that clearly affected the surface wettability of the coating. The pristine silica nanoparticle (20 mg/ml in DMF) coating and PMMA (20 mg/ml in DMF) coating could exhibit WCA less than 90°. Fig. 4 shows the effect of silica concentration in PMMA on the wetting properties of the coating. The SP-1 sample exhibited a WCA of nearly 124° due to its smooth morphology that could not able to trap air pockets. A water drop strongly adhered on the coating surface, even after tilting the coating surface upside down. Similarly, in the case of a SP-2 sample, besides exhibiting a WCA of nearly 140°, it falls in Wenzel wetting state. The air trapping in the rough microstructure of SP-3 sample facilitated reduced adhesion between the water droplet and coating surface. A water drop sits on the composite air/solid interface with WCA higher than 168° that rolled off at a small disturbance. At higher loading of silica nanoparticles in PMMA, SP-4 sample revealed decrease in WCA of 154° due to the micrometer scale voids present in the loosely connected aggregated grains of silica-PMMA nanocomposite. The water drop could have intruded inside the big voids while still sitting over the composite air/solid interface. However, the SP-4 samples were fragile in nature and simple fingertip touching could take off the coating. The silica nanoparticles provided effective surface roughness whereas the PMMA contributed in lowering the surface free energy of the coatings.

The self-cleaning property and mechanical stability of the SP-3 samples were tested (Fig. 5). Fig. 5a shows the optical photograph of water drops on SP-3 sample. Few water drops were colored with methylene blue to achieve clear view. The water drops (~ 8 μL) placed at different positions on the sample exhibited spherical shape with average WCA of 168°. The self-cleaning ability of the coating was checked by simply spreading carbon dust particles on the surface and subsequently rolling water drops on it [22]. As shown in Fig. 5b, the water drops effectively cleaned the surface by easily picking up the carbon dirt particles. A small shaking resulted in rolling off the carbon collected water drops from surface. Thus, the coating demonstrated good self-cleaning ability. Also as shown in Fig. 5c, the coating was mechanically sustained against the water jet impact [23]. A water jet hit the coating surface and rebounded without affecting the wettability of the surface.

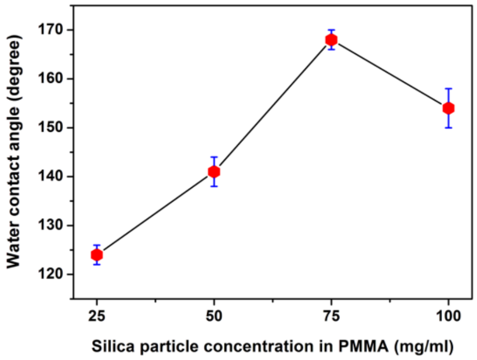

Fig. 4 – Variation of WCA of the coatings with increasing concentration of silica nanoparticles in PMMA

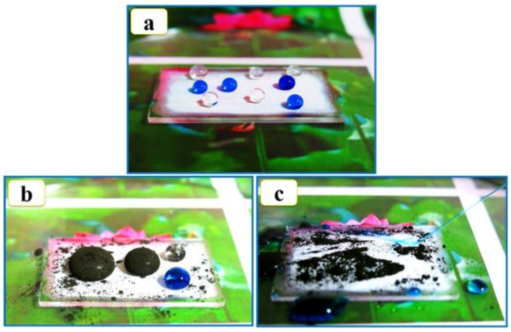

Fig. 5 – Photographs of water drops (a), self-cleaning ability (b) and water-jet impact test on SP-3 sample (c)

4. CONCLUSIONS

The self-cleaning superhydrophobic coatings were successfully fabricated by facile drop casting method. At lower loading of silica nanoparticles, polymer structure dominates resulting smooth morphology, whereas for higher loading of silica nanoparticles, powder like fragile coating was obtained. The optimum content of silica nanoparticles in PMMA structure was controlled to attain rough microstructured superhydrophobic coating with water contact angle higher than 168°. The obtained superhydrophobic coatings exhibited good self-cleaning ability and mechanical durability. Due to high micrometer scaled surface roughness, the coatings were opaque in appearance and might not show good mechanical durability against sandpaper or taber abrasion tests. The high optical transparency of the coatings can be achieved by controlling the size and aggregation of silica nanoparticles.

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