



Preparation of Superhydrophobic Coating Using Silica–PMMA Nanocomposite

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Lotus leaf shows high water repellency due to its hierarchical rough structure and thin layer of low surface energy material on it. In this work, superhydrophobic coatings are prepared by silica-polymethylmethacrylate (PMMA) nanocomposite on a glass substrate using a cost effective and simple dip-coating method. The superhydrophobicity of the coatings is controlled by varying the concentration of PMMA in the nanocomposite. At optimum concentration of PMMA, coating shows water contact angle of $155 \pm 3^\circ$ with a rolling angle of 7° as a result of development of rough microstructure. The stability of the coatings is examined by finger wiping, water jet impact, and adhesive tape test. These superhydrophobic coatings can be used in various industrial applications.

1. Introduction

The water repellent property of the coating surface depends on the surface chemical structure and the roughness.^[1] In nature, water strider's legs,^[2] animal furs,^[3] lotus leaves,^[4] cicada orin's wings^[5] possess high water repellent property. The surface showing water contact angle (WCA) more than 150° and sliding angle less than 10° are identified as superhydrophobic surface. The appearance of the wax-like coating on hierarchical rough structure may be the cause of the high WCA and a very low sliding angle of lotus leaves.^[6] High water repellent coatings are remarkable in various industrial applications such as self-cleaning,^[7,8] oil-water separation,^[9–11] anti-icing,^[12] and drag reduction.^[13] The various methods for the manufacture of superhydrophobic coating have been reported in the last two decades, such as sol–gel processing,^[14–16] electrochemical deposition,^[17] phase separation,^[18] Emulsion,^[19] plasma method,^[20] template method^[21,22] and etc.^[23–25]

Zhengwei et al.^[23] have prepared transparent superhydrophobic films with superior thermal stability and moisture resistant films without the usage of dibutyltin laurate (DBTL). Kavale

et al.^[11] have optimized optically transparent, superhydrophobic methyltrimethoxysilane based silica coatings on glass substrate at room temperature without silylating reagent using simple dip-coating technique. Yoon et al.^[26] have developed a highly transparent self-cleaning, optically transparent, robust superhydrophobic surface by organosilane-coated alumina particles deposited on glass plates by an easy electrospray technique. Latthe et al.^[27] have developed the sol–gel processed semi-transparent and self-cleaning superhydrophobic coatings that have been successfully prepared under a small loading of PMMA in silica and the coatings showed improved hydrophobicity, optical

transparency and scratch resistance. Ahmad et al.^[28] have synthesized the antireflective superhydrophobic silica thin films on a glass substrate by a sol–gel dip-coating method which showed self-cleaning and anti-icing properties. Latthe et al.^[29] have fabricated the transparent superhydrophobic silica film and studied the effect of surface-modifying agents on the water repellent behavior of a silica surface. Haranath et al.^[30] have described the effect of methyltrimethoxysilane (MTMS) as a precursor on the hydrophobicity and some physical properties of silica aerogels with negligible volume shrinkage.

In this present work, we have prepared superhydrophobic coating on a glass substrate using silica–PMMA nanocomposite by a facile dip-coating method. These coatings exhibited WCA $155 \pm 3^\circ$ with a rolling angle of 7° .

2. Result and Discussion

2.1. Wettability and Surface Morphology of Coating

The surface wettability of the coating was controlled by the concentration of PMMA in alcosol. The alcosol was prepared by adding MTMS in ethanol and ammonium solution. A simple deposition of alcosol on a glass slide exhibits a WCA of $126 \pm 3^\circ$. After adding PMMA into alcosol, WCA was found increased. The S1 and S2 samples exhibited the WCAs of 135° and 143° , respectively due to their smooth surface morphology which cannot effectively trap the air pockets and hence the contact area of water to solid surface is high. A S3 sample exhibited a WCA of $155 \pm 3^\circ$ for every water drop put at different locations on the sample as shown in **Figure 1a**. Actually, the S3 sample might have uniformly dip coated on the glass substrate; however, after heating at 100°C , the notable small cracks were developed in the coating

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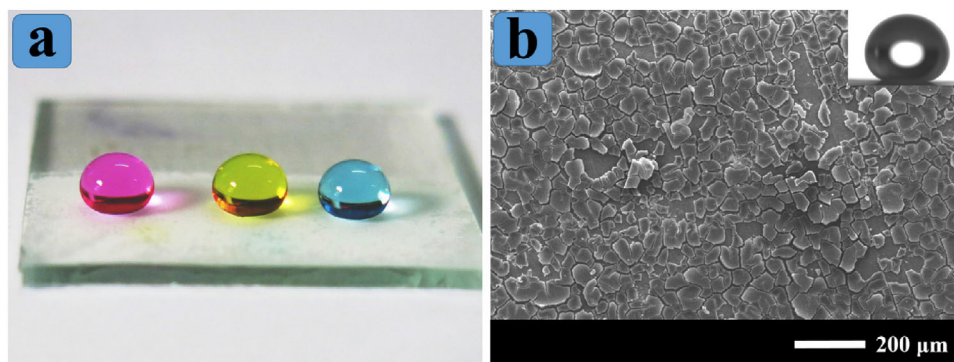


Figure 1. a) The dyed water drops on S3 sample, b) SEM micrograph of S3 sample.

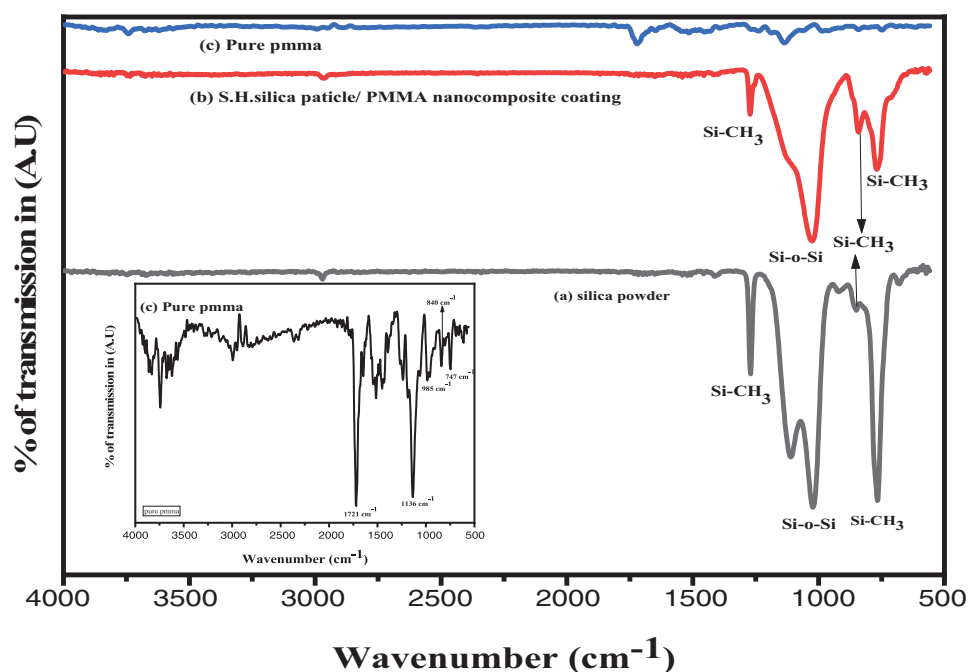


Figure 2. Fourier transform infrared spectra of a) silica powder, b) silica–PMMA nanocomposite and c) pure PMMA.

as a result of fast evaporation of solvent from the coating surface. The crack development in the coating might be responsible for the superhydrophobicity of the coating because the tiny air pockets can trap in the rough structure developed by the cracks. It was also worth noting that, the S3 sample without heating at 100 °C showed WCA of 130°. Hence the crack development at 100 °C was found helpful to achieve superhydrophobic property in the coating.

2.2. Fourier Transform Infrared Spectroscopy Studies of Coating

The chemical composition of silica powder, silica–PMMA nanocomposite and pure PMMA were characterized by the FT-IR spectroscopy. The characteristic absorption peaks observed in the range 500–4000 cm^{-1} indicates the presence of methyl groups as shown in Figure 2. Figure 2a represents the Fourier transform infrared (FTIR) spectra of silica powder.

The absorption peak at 1080 cm^{-1} corresponds to a Si–O–Si asymmetric stretching vibration.^[1] The normal bending of the C–H bond observed at 2971 cm^{-1} . The peaks at 765 cm^{-1} and 1270 cm^{-1} indicates the presence of Si–CH₃ bonds.^[31] Figure 2b represents FTIR spectra of silica–PMMA nanocomposite. The absorption peak at 1074 cm^{-1} corresponds to a Si–O–Si asymmetric stretching vibration^[32] The stretching and normal bending of the C–H bond observed at 2971 and 1272 cm^{-1} and the peaks 769 and 841 cm^{-1} indicates the presence of Si–C bonds.^[33,34] The FTIR spectra of the PMMA is as shown in Figure 2c. The peak observed at 1150 cm^{-1} represents C–O–C stretching vibration. The absorption bands observed near 843 and 976 cm^{-1} are due to specific absorption vibration of PMMA. The absorption band observed at 754 cm^{-1} corresponds to the α -methyl group vibrations. The existence of the acrylate carboxyl group was confirmed by the absorption band observed at 1725 cm^{-1} .^[27]

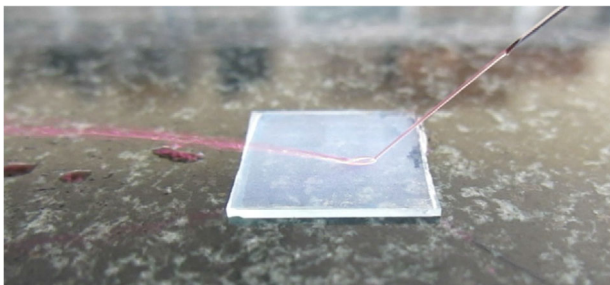


Figure 3. The optical image of water jet impacting on S3 sample.

2.3. Durability of Coating

A durability of the superhydrophobic coating is an important parameter to find its application in industrial use. Generally, the durability of superhydrophobic coating was characterized by finger wiping, water jet impact, and adhesive tape test. The wettability of the S3 sample was checked after wiping by fingertip. The tested S3 sample showed the same WCA after fingertip wiping test. The stability of the coating was also evaluated by spraying the water jet on it. The jet hits on coating with normal speed for more than 1 min, the continuous bouncing of water jet confirms that coating was highly stable for jet impact test. The continuous bouncing water jet is shown in **Figure 3**.

The adhesive tape was placed on the S3 sample and smoothly pressed by fingertip to make good contact. The tape was peeled off to test the mechanical durability of the coating. The WCA showed the same value up to 5 cycles of adhesive tape test. After that coating gets damaged and superhydrophobicity starts to vanish. After 15 cycles of adhesive tape test, coating was completely removed and the surface becomes hydrophilic nature.

3. Conclusion

In summary, we have successfully prepared superhydrophobic coating through dip coating the glass slides from silica–PMMA nanocomposite. The superhydrophobicity in the coatings were achieved by optimizing the concentration of PMMA in the nanocomposite and heat treatment. The prepared superhydrophobic coating exhibited a WCA of $155 \pm 3^\circ$ with a rolling angle of 7° . The finger wiping test and water jet impact test revealed the mechanical stability of the coating. It was also recognized that, the coatings were not stable against harsh mechanical tests like adhesive tape test. The durability and transparency of the coating can be further improved by checking the compatibility of other polymers in combination with silica.

4. Experimental Section

Materials: Methyltrimethoxysilane (MTMS, 98%) was purchased from Sigma Aldrich, USA. *N,N*-Dimethylformamide, poly(methylmethacrylate) (PMMA ~120000), ammonia solution and ethanol were purchased from Spectrochem Pvt. Ltd. Mumbai, India. Glass slides were obtained from polar industrial corporation Ltd. Mumbai, India.

Preparation of the Super Hydrophobic Coating: At first, a mixture of 25 mL ethanol and 1 mL ammonia solution was magnetically stirred. After 15 min of constant stirring, 1 mL of MTMS was added dropwise and

stirring further continued for 1 h. Meanwhile, 3 mg mL⁻¹ PMMA solution in DMF was prepared. The various volumes of PMMA solutions such as 2, 4, and 6 μ L were added into the above solution to prepare silica–PMMA nanocomposite and labeled as S1, S2, and S3 samples, respectively. After 4 h of stirring, a clean glass slide was dipped into the solution for 2 min. The dipping and withdrawing speed (5 mm s⁻¹) was controlled by the dip-coating machine. The dip-coated glass slides were annealed at 100 °C for 2 h in the oven.

Characterizations: The surface morphology of the coating was examined by scanning electron microscope (SEM, JEOL, JSM-7610F, Japan). The chemical structures of the coating were studied by Fourier transform infrared spectroscopy (BRUKAR, Model No. ALPHA 100508). The contact angle meter was used to measure the WCA (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd. India). The stability of the coating was investigated by finger wiping, water jet impact, and adhesive tape test.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Coatings, lotus leaf, nanocomposite, superhydrophobic

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