Progress in Organic Coatings 122 (2018) 170–179

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Preparation of transparent and robust superhydrophobic surfaces for self-cleaning applications

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ARTICLE INFO

Keywords:
Superhydrophobic surface
Self-cleaning surface
Mechanically robust coatings
GLYMO
Silica particles

ABSTRACT

Superhydrophobic surfaces have recently attracted a lot of attention due to their high water repellency along with a wide range of applications in many fields. The application of such surfaces for self-cleaning purposes, such as in solar cell modules, has been limited due to the lack of mechanical robustness, thermal stability and ultraviolet radiation resistance. The fabrication of superhydrophobic water-repellent surfaces with mechanical robustness and high transmittance remains a major challenge. This paper presents a method for fabrication of transparent, robust and stable superhydrophobic surfaces by simple spray coating process. The developed coating solution can be sprayed on all kinds of materials to create a superhydrophobic self-cleaning surface. Proper molar ratios of Methyltrimethoxysilane (MTMS) and (3-Glycidyloxypropyl)trimethoxysilane (GLYMO) are used to bond the functionalized silica nanoparticles to various substrates and promote robustness. Optimum spraying cycles (layers) of 1.0%wt SiO_2 nanoparticles after adhesive layer has resulted in contact angles of the order of 170° with a hysteresis of 6° and sliding angle of 1°. Developed surfaces also exhibited excellent stability under pressurized jet water, abrasion and ultraviolet radiations. Improvement of surface transmittance was achieved by annealing the surface under temperatures up to 300 °C without losing superhydrophobicity. The optical transmittance of the optimum annealed surface varied between 75% of that of virgin glass, at the visible light wavelength of 400 nm and 90% at 800 nm. The unique combination of the above-mentioned desired properties of the fabricated surface, makes them a promising candidate for outdoor self-cleaning applications even under harsh environmental conditions.

1. Introduction

Superhydrophobic surfaces have many applications across a wide range of areas, including self-cleaning [1,2] anti-corrosion [3,4], anti-icing [5] and drag reduction during fluid transportation [6,7]. Mechanically robust and transparent superhydrophobic surfaces have potential applications for self-cleaning purposes in solar PV panels and other optical fields.

Surfaces having high water contact angle and low sliding angle as well as low hysteresis are desired for having high water repellency. It is a well-known fact that the hydrophobicity of a surface is governed by the surface chemistry [8–10] and surface roughness [11,12]. Low surface energy associated with micro and nano roughness can create superhydrophobic surfaces [13,14]. The nano scale roughness of these surfaces can significantly lower the contact area between surface and water. Water droplets remain perched on such surfaces with trapped air within the asperities valleys below the water droplets, thus resulting in very high water contact angle. With the deep understanding of the superhydrophobic surface nature, researchers have developed artificial superhydrophobic surfaces by creating hierarchical surface structures using different methods such as sol-gel [15–17], electro- spinning [18,19] and plasma/laser etching methods [20,21].

Gao et al. [22]. developed superhydrophobic surfaces with hierarchical structure using Polydimethylsiloxane (PDMS) and silica particles deposited onto glass slides. They found that 14 nm particles sizes result in higher contact angle than 7 nm particles sizes, due to the regularity of its micro- and nano-structure. Silica particle-PDMS surface with 7 nm has more grooves and irregularities which minimize the amount of air pockets to maintain the water droplet. Jin et al. [23] developed hierarchical-structured superhydrophobic surfaces using PDMS by casting and laser etching. The resulted surface texture is micro-submicron-nanostructures which is generated by micropillars and submicron-nano grooves and with static and dynamic water contact angles 162° and < 5°, respectively. Some researchers reported that by

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https://doi.org/10.1016/j.porgcoat.2018.05.018
Received 14 September 2017; Received in revised form 7 May 2018; Accepted 10 May 2018

using commercially available abrasion resistance silicone resin improves the abrasion resistance of the superhydrophobic surfaces [24,25]. This is often used with a coupling/bonding agent to increase the adhesion between the substrate and thin layers [26]. Water-repellent surfaces prepared by sol-gel route suffer from some major drawbacks that severely limit their large-scale outdoor applications. The most notable of these are poor mechanical properties that include weak adhesion to substrate and low wear/abrasion resistance, and fast degradation under UV radiation due to vulnerability to long-term UV exposure of polymers. In this regard, development of water-repellent surfaces with improved mechanical stability/robustness and good resistance to long-term UV weathering are the major challenges. Hence, in depth research is needed to address these issues and overcome the above-mentioned challenges as well as not compromising on the transparency.

In this work, we successfully developed a transparent, and mechanically robust superhydrophobic MTMS/GLYMO/SiO_2-PFOTS coating by sol-gel technique. The product can be easily applied by spray coating on different kinds of substrates to create superhydrophobic surfaces with very high water contact angles and low hysteresis. The fabricated surfaces exhibit outstanding mechanical stability under water jet, and sand paper abrasion. The developed coating with its excellent thermal stability, and self-cleaning performance has great potential for outdoor practical applications.

2. Experimental procedure

2.1. Materials

Silicon dioxide (SiO_2,10–20 nm), Methyltrimethoxysilane (MTMS), (3-Glycidyloxypropyl) trimethoxysilane (GLYMO), 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane (PFOTS), Ethanol, Acetone, and Ammonia were purchased from Sigma-Aldrich (Germany) and used as received. The deionized (DI) water used during the experiment was collected from the Milli-DI® Water Purification System.

2.2. Preparation of coating solution

Coating solution A (referred to as Sol A) was prepared by dropwise adding of 2 ml of GLYMO, 2.58 ml of MTMS, 1.47 ml of DI water, and 0.5 ml of Ammonia into 10 ml of Ethanol solvent and stirring for 1 h. Coating solution B (referred to as Sol B) was prepared by adding silica nanoparticles into ethanol solvent before adding 150 µl of PFOTS. The bottle cap must be kept tight to prevent oxidation of PFOTS by air. The solution in the small bottle was sonicated in ultrasonic bath for 2 h. According to the amount of silica nanoparticles and ethanol, a different weight percentage of silica nanoparticles (0%, 0.5%, and 1%) functionalized by PFOTS in Ethanol solvent can be prepared. After that, Sol B was kept in a sealed bottle before using it as second layer after the first layer of Sol A.

2.3. Deposition of the coating solution

First, Sol A was sprayed on the glass slides using 3 cycles. A cycle is achieved by manually spraying the glass surface by traveling left-to-right and back at a constant speed. After completion of Sol A deposition, the samples are carefully put in the oven at 80 °C for 2 h to evaporate the Ethanol solvent completely. This first coating layer serves as a binder. After that, the glass slides are immediately sprayed with a second layer of Sol B to functionalize the surface as well as to create roughness, as illustrated in Fig. 1. This second layer of functionalized silica nanoparticles are chemically bonded and imbedded in the first layer to create surface roughness as well as provide low surface energy. After the deposition of the second layer, the samples are kept at room temperature for 24 h for the proper aligning and arrangement of low surface energy functional groups ($-CF_2$, $-CF_3$) [27].

Following this, the surface becomes chemically stable and water contact angle measurement can be conducted. Different spray cycles (1–5 cycles) of Sol B with different weight percentages (0–1 wt%) of silica (SiO_2) are applied. More details about the technique can be found in the MSc thesis by A. Bake [28]. The resulting samples identification is illustrated in Table 1.

2.4. Characterization

A contact angle goniometer (Kyowa Interface, Inc. Japan) is employed to determine the static water contact angle, sliding angle, and advancing and receding contact angle. The sessile drop model is used with the tangential method to measure the static water contact angles (CA), sliding angle (SA), advancing angle (AA), receding angle (RA), and hysteresis (H) in a proper manner. Approximately, 10 µl water droplets are carefully placed on the surface and the angle is measured from the captured image [16]. Measurements, from different locations on the surface, are repeated at least 5 times for each sample to obtain a representative average value. UV–vis spectrophotometer (JASCO, V-670) is used to measure the transmittance of the spray coated glass slides in the visible light wavelength range of 400 to 800 nm. The surface topography of the coatings is investigated using a 3-D profilometer and a Field Emission Scanning Electron Microscope (FESEM, TESCAN). The elemental composition of selected locations is analyzed using Energy Dispersive Spectroscopy (EDS). Survey scan and high-resolution XPS spectra of C 1 s are recorded using Thermo-Scientific Escalab 250Xi spectrometer. The Raman spectra of selected samples are recorded with DXR Raman Spectrometer (Thermo Scientific) using a 455 nm laser source. FTIR spectra are obtained using a Nicolet is50 spectrometer (Thermo Scientific) with an ATR accessory.

2.5. Durability and robustness tests

The coated surfaces are tested for thermal stability at the temperatures of 300 °C, 350 °C and 400 °C. This is achieved by placing at least three samples per temperature level in a pre-heated oven for 2 h for annealing. Glass slides (both coated and uncoated) are tilted to 10° and sand particles are sprayed to investigate the self-cleaning performance of coated glass slides. OmniCure S2000 UV spot curing system (EXCELITAS TECHNOLOGIES) is used to study the UV resistance of the coating and OmniCure R2000 radiometer is employed to measure the light intensity reaching the surface of the coated glass substrate. The coated samples are tested under a UV light intensity of 250 mW for 10 h and followed by exposure to a very high UV light intensity of 3000 mW for 2 h. Water jet test schematic is illustrated in Fig. 2 (a). Water is pumped at the rate of 1.0 L/min through a 4 mm diameter tube; impacting the coated glass surface, placed 15 cm below it, at an approximate speed of 4.25 m/s. Abrasion test is conducted as illustrated in Fig. 2 (b). Sample is placed on the BUEHLER 240 GRIT size sandpaper with the coated surface in contact with the sand paper and on top of glass surface placed 100 g of weight. In the first step, the sample traveled a distance of 10 cm on the sand paper and the glass slide horizontally is rotated 90°. In the second step, it traveled back to original position with traveling distance of 10 cm. These two steps are considered as one cycle. Total of 5 cycles of abrasion test are conducted that is corresponds to a total traveling distance of 100 cm. According to the glass piece size of 25 × 25 mm and 100 g of weight on it, applied pressure on the surface during the test was about 1.6 kPa.

3. Results and discussion

3.1. Wettability of surfaces

The results of Fig. 3 (a) shows that, independent of number of cycles, Sol B without addition of silica nanoparticles does not bring any significant increase in the static contact angle. Thus 1–2 spray cycles of