



Mechanically robust polyvinylidene fluoride (PVDF) based superhydrophobic coatings for self-cleaning applications

Divya Kumar^a, Lin Li^b, Zhong Chen^{a,*}

^a School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

^b School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

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ABSTRACT

The demand for effective self-cleaning, water repellent coatings has been growing over the years. Achieving superhydrophobic coatings with good mechanical durability has always been a key challenge. In this work, superhydrophobic surface was created by introducing silica nanoparticles in a polyvinylidene fluoride matrix (PVDF). The combination of a fluorinated polymer matrix and inorganic particulate fillers (SiO₂) and surface functionalizing agent aminopropyltriethoxysilane (APTES) produced coatings with improved mechanical properties and good adhesion with the substrate. The static contact angle (CA) of the composite coating with PVDF: SiO₂ = 1: 1 by weight was found to be 154° with a sliding angle of <2°. The mechanical properties of the coating, particularly hardness and Young's modulus, effect of accelerated erosion and coating adhesion have been studied in detail. The effect of UV weathering on the coated surfaces is also tested. A simple self-cleaning test based on spectrophotometry is applied to quantitatively measure the self-cleaning performance of the coatings. The described coating process is simple and can be effectively scaled up for large structure protection.

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1. Introduction

Superhydrophobic surfaces have been of great interest to both the industrial and scientific community in recent times. Such water repellent coatings with a static contact angle (CA) greater than 150° and low sliding angle (SA) are highly desirable for anti-corrosion, anti-icing, self-cleaning and anti-slip applications. Superhydrophobic surfaces have been prepared using different methods like sol-gel synthesis, chemical vapor deposition, lithography etc., and varying degrees of success has been achieved in the past [1–11]. Mimicking the combination of hierarchical roughness and low surface energy similar to that of the lotus leaves results in surfaces with good hydrophobic and superhydrophobic properties [12–15]. The main disadvantage of some of the methods is that they cannot be scaled up easily for many practical applications or the cost is too high. Generally, the methods used to prepare superhydrophobic surfaces can be classified as top down or bottom up approaches. These approaches mainly involve creating rough surface from a low surface energy material or roughening a low energy surface respectively [15–20]. Fluorinated polymers like Teflon are of special interest because of their inherently low surface energy [16]. But

there are few solvents in which Teflon is readily soluble therefore, other fluorinated polymers like polyvinylidene fluoride (PVDF) and other perfluoroalkyl polymers can be used instead. PVDF being a thermoplastic is quite stiff and has good chemical stability. One of the disadvantages of PVDF based coatings is that they have poor adhesion with most substrates. Therefore, pre-treatment of the surfaces is required. Basu et al. and Yan et al. have previously studied PVDF based coatings with hydrophobically modified silica and CaCO₃ [8,9]. But these works have not reported the mechanical durability and performance of the coatings under erosive/abrasive environments. The poor adhesion of several PVDF based coatings is also an area of concern [9]. In this work, we describe the preparation of PVDF based superhydrophobic coatings with good mechanical properties and self-cleaning performance, as well as improved adhesion to the substrate. This paper addresses the gap by investigating the effect of various simulated environmental conditions, such as weathering and erosion wear, on the coating performance. A simple solution to improve coating adhesion is explained. 3-Aminopropyltriethoxysilane (APTES) and fluorinated alkyl silane (FAS) are used as surface functionalizing agents in order to improve the adhesion of the coating to the substrate and to lower the surface energy, respectively. Silica nanoparticles are introduced to increase the roughness of the coatings. The resulting coatings show improved hardness and Young's modulus. The coatings also adhere very well to the glass substrate. The self-cleaning test based on

* Corresponding author.

E-mail address: ASZChen@ntu.edu.sg (Z. Chen).

spectrophotometry used in our previous work is used to measure the self-cleaning performance of the coatings [21]. Coatings with PVDF: SiO₂ = 1:1 by weight was found to have a self-cleaning efficiency of 97.6%.

2. Experimental

2.1. Materials and coating preparation

The coating system consists of PVDF as the matrix, *N,N*-dimethylformamide (DMF) as the solvent, APTES as the surface functionalizing agent and Perfluorodecyltriethoxysilane (FAS-17) as the hydrophobic modifier. Surface roughness was introduced by the addition of silica nanoparticles of 10–20 nm average particle size. Ethanol (EtOH) and DI water were used as solvents. All the chemicals were purchased from Sigma Aldrich and used without any further modification.

5 and 10% PVDF solutions were prepared by dissolving it in DMF and heating the mixture at 50 °C. 10–20 nm silica particles were dispersed in a trimolar solution of hydrolyzed FAS. This solution was then added to the PVDF solution at PVDF: SiO₂ = 1:0.5 and 1:1 by weight and stirred for 24 h. A 5 mM solution of APTES in EtOH was prepared. The glass slides were first cleaned by ultrasonication with EtOH and DI water and then immersed in the 5 mM APTES solution for 24 h. After 24 h, the glass slides were again washed with DI water and the various PVDF coatings were applied by using a spray gun at a pressure of 3 bar from a distance of 10–25 cm. Glass slides not treated with APTES were also coated with the PVDF solutions for comparison. The coated slides were allowed to dry at room temperature for 1 h and then cured at 80 °C for 3 h.

2.2. Characterization of the coatings

The hydrophobic properties of the coating were characterized using the water contact angle (CA) and sliding angle (SA). The CA and SA were measured using the Dataphysics OCA 20 Contact angle instrument. Droplets of volume 1 and 5 μL were used for measuring the CA and SA respectively. The reported results are the average values of CA and SA measured over five distinct points on each sample. Three coated samples were tested under each coating category.

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the surface chemical bonds. The ATR method was used to confirm the presence of functional groups that impart the hydrophobic functionality to the coatings.

The surface topography and the arithmetic average roughness values (*R_a*) of the coatings were studied by Atomic Force Microscopy (Digital Instruments). Field emission scanning electron microscope (FESEM) images were obtained to study the surface morphology.

The cross-cut adhesion test according to ASTM D 3359-09 was used to measure the extent of adhesion of the coatings to the substrate. This test can also provide an evaluation of the brittleness of the coatings by observing the damage patterns along the cut lines. The hardness and Young's modulus of the coatings were measured using a nanoindenter under a constant load of 1.3 mN over a depth range from 500 to 1500 nm.

The effect of erosive wear is characterized by measuring the weight, roughness, thickness, CA and SA after micro-sand abrasion. Particles of grit size 63 μm (220 mesh size) were blasted on to the coated surfaces from a distance of 10 cm at a pressure of 200 kPa for 30 s. The exposed area for the sand erosion was 2.43 cm². The test is based on ASTM F1864 which is used to test resistance of plastics and coatings to surface erosion as a result of dust impingement. The test was repeated on three samples under each category.

UV weathering tests were performed by placing the sample in a weathering chamber (ATLAS instruments) following the test standard by ASTM G154-12a. The procedure involves 4 h of UV exposure, followed by 4 h of water spray and condensation. The UV/water cycle was repeated over a period of 72 h. Eight UV lamps (295–400 nm), each having the power intensity of 1.2 W/m², were used.

To evaluate the effectiveness of the coatings for self-cleaning applications, a spectrophotometer was used to monitor the change in lightness values. The lightness reading here refers to the luminance or the tone perceived by the spectrophotometer on the samples. The coatings were sprayed with artificial dirt and then subjected to cleaning using a controlled water spray. The lightness (*L*) value was measured by the spectrophotometer at three stages of the self-cleaning test: before the spray of the artificial dirt solution (*L*₁), after the dirt was dried (*L*₂), and after dirt was cleaned using spray of clean water (*L*₃). The *L* values were measured over five fixed points over each sample. The degree of dirt accumulation and self-cleaning efficiency were calculated based on the lightness values and compared among different coatings. An artificial dirt mixture composed of 85% nano clay, 10% silica particles (10 μm), 1% carbon black, 2% oil, and 2% salts (all values measured in weight percentage) was used to test the coatings. The mixture was dispersed in water at a concentration of 15 g/L. It was then sprayed onto the coated substrates from a distance of 25–30 cm at a pressure of 3 bar using a spray gun. The dirt coated samples were allowed to dry overnight. These samples were then subjected to clean water spray under the same spray condition. All samples were placed on a white background during the spectrophotometric measurement.

3. Results and discussion

3.1. Contact angle and sliding angle

Fig. 1a shows the change in CA of the coatings at different concentrations of PVDF and nanosilica loading. PVDF was fixed at 5% and 10%, and the PVDF:SiO₂ ratio was at 1:0.5 and 1:1. The results are compared with PVDF coatings without silica filler. The CA increases with increase in filler loading, and the trend is very similar for both concentrations of PVDF. The highest CA of 159.16 ± 1.38° was achieved in the coating with 10% PVDF with the highest silica loading. The high CA can be attributed to the dense clustering of the silica particles on the coating surface leading to hierarchical roughness.

The CA, SA and average surface roughness (*R_a* – arithmetic average) values are listed in Table 1. From the values in Table 1 and Fig. 1b it can be seen that the SA decreases with increasing *R_a* caused by increasing nanosilica filler content. 10% PVDF coating with the highest silica loading has a SA < 1° indicating a case of heterogeneous wetting [20]. On coatings that have no silica fillers or lower concentration of fillers, the wetting regime is more homogenous resulting in higher SA [21].

3.2. FTIR analysis

The FTIR spectrum of the coatings with 10% PVDF with different concentrations of filler loading is shown in Fig. 2a. The prominent dips (peaks) observed around 1680–1620 cm⁻¹ corresponds to C=C from the PVDF. The C–F stretch bonds from FAS contribute to the peaks found at 1000–1400 cm⁻¹ [22]. A separate FTIR spectrum was collected on glass coated with APTES. From spectrum in Fig. 2b, the presence of APTES is confirmed by the peak at 1600 cm⁻¹ resulting from the bending of the N–H bonds and the broad band around 1000 cm⁻¹ is due to the stretching of Si–O–Si bonds. This confirms that the substrate surface was successfully functionalized by the

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