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Superhydrophobic coatings based on colloid silica and fluorocopolymer

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ABSTRACT

Superhydrophobic coating system was developed with colloidal silica and crosslinkable fluorocopolymer as filler and matrix respectively, to yield low surface energy and chemical stability, high hardness, and strong adhesion with substrates. The effects of particle surface functionalities, volume fraction and dimension on hydrophobicity and integrity of coatings were systematically investigated. The coating performance was closely dependent on these three factors. Superhydrophobicity (water contact angle ~155° and rolling angle ~ 1°) and desired integrity was observed in the coatings with fluorinated particles (with dimension of either 340 or 1450 nm) at optimal particle volume fraction of 60%.

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1. Introduction

"Lotus effect" that the lotus leaves can be cleaned by rain is a mysterious phenomenon in nature. Barthlott and his co-works discovered the secret behind in 1997 [1,2]. Lotus leaves are covered by many papillae with diameters ranging from 3 to 10 μm, while these papillae are decorated with protrusions of hydrophobic epicuticular wax on nanometer scale. Such a micro-nano-binary structure (MNBS) promotes the surface roughness significantly, and the air trapped in the grooves minimizes the contact area with water, while the hydrophobic wax protrusions prevent the lotus leaves from wetting. The water droplet on the lotus leaf possesses pearl like shape, and can roll easily. The contaminants on the lotus leaf can be therefore cleaned with water. Academically, when contact angle of water exceeds 150°, the surface is termed "superhydrophobic", and further, when the roll-off angle is less than 5°, the surface is called "self-cleaning" or under "lotus effect". In recent years, self-cleaning surfaces have been attracting remarkably increasing interest because of its intrinsically high contact angle and low roll-off angle [3–10]. This kind of self-cleaning surface plays an important role in many applications, such as self-cleaning windows [11,12], interior and exterior wall of the buildings [13–15], drag-reduction [16–18], microfluid channels with reduced friction [19–21], anti-icing coating on the aircraft [22,23], etc.

The surface chemistry and roughness are two primary factor determining superhydrophobic surface. Surface with lower surface energy and higher degree of roughness possesses better hydrophobicity, and even superhydrophobicity [24–26]. It is well known $-CF_3$ group has the lowest surface energy in the world, and water contact angle on its flat surface is only 120° [27]. However, when the MNBS roughness is introduced, the water contact angle become 160° with a roll-off angle <5°. Typically superhydrophobic surfaces were created by changing the surface chemistry to reduce surface energy or by increasing the surface roughness via surface texturing or by combining both [28]. Surface texturing may be cumbersome, expensive, and may be difficult to achieve for large and complex articles [29]. Surface modification is one of the most feasible techniques to fabricate superhydrophobic surface [30], which is typically performed by spraying the substrate with a super-hydrophobic coating, layer or a film [31]. Coating the substrate with a superhydrophobic coating is a very efficient strategy of converting

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any substrate into a superhydrophobic surface. However, most of such superhydrophobic coatings suffer from poor adhesion to the substrate, lack mechanical robustness, and are susceptible to scratches. Effort is therefore sought to fabricate superhydrophobic coatings with controlled hydrophobicity, good durability. A method was recently described by Xue et al. [32] that Superhydrophobic surfaces were fabricated via surface-initiated atom transfer radical polymerization of fluorinated methacrylates on poly(ethylene terephthalate) (PET) fabrics. Superhydrophobic property and excellent chemical robustness were observed on the fabrics, even after exposure to various of chemicals, such as acid, base, salt, acetone, and toluene. Nevertheless, these structures are also not feasible for commercial applications due to its complicated fabrication process.

In this paper, a coating system based on fillers and polymer matrix was developed by mixing colloidal silica with a cross-linkable fluorocopolymer at ambient temperature followed by spray (Fig. 1). Here, fluorinated ethylene-(hydroxyl-alkyl)vinyl ether (FEVE) copolymer was selected as polymer matrix due to its good hydrophobicity, mechanical properties, weatherability and solubility. Functionalized colloidal silica was used as fillers. The coating possessed very good super-hydrophobicity and durability. This process was straightforward and practical for potential commercial applications in addition to its superior properties. Fundamental understanding of the effects of particle surface functionalities, volume fraction and dimension on hydrophobic performance and coating integrity was systematically investigated. Further study to identify the low cost materials for silica functionalization and low cost polymer matrices is needed for real commercial applications.

2. Experiment

2.1. Materials

All solvents were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Tetraethyl orthosilicate (TEOS) was obtained from Hubei Wuhan University Silicone New Material Co., Ltd (China). Colloidal silica with particle size of 90 nm (dispersed in isopropanol with concentration of ~30 wt.%) was purchased from Fuso Chemical Co., Ltd. (tridecafluoro-1,1,2,2-tetrahydrooctyl)methyldichlorosilane and hexamethyldisilazane were purchased from Gelest, Inc. and Aldrich, respectively. Fluorocopolymer and hexamethylene diisocyanate (HDI) were supplied by Xuzhou Zhangyan Fluoro Chemical Co., Ltd (China).

2.2. Synthesis of colloidal silica

Colloidal silica with particle size of 340 and 1450 nm was synthesized by Stober method. Typical procedures for preparing 340-nm silica were described as follows. 70 mL ethanol and 50 mL ammonia was contained in a 250 ml round bottom flask, and magnetically stirred at speed of around 1000 rpm to facilitate ensure good mixing. Then, 4 mL TEOS was slowly added with pressure-equalizing addition funnel, and the mixture was stirred for additional 48 h to complete hydrolysis and condensation reaction of TEOS. The above mixture were centrifuged at speed of 2000 rpm for 30 min, and the precipitates (silica particles) were thoroughly washed with distilled water followed by centrifugation repeatedly. Finally, colloidal silica was preserved in distilled water, but centrifuged and dispersed in methylisobutylketone prior to further chemical functionalization. 1450-nm colloidal silica was synthesized by similar procedures.

2.3. Preparation of fluoro or methyl functionalized colloidal silica

Typical procedures for preparing fluoro-functionalized colloidal silica (340 nm) were described as follows. 100.0 g toluene containing dispersed colloidal silica (concentration: 12 wt.%) and 100 g dichloromethane were mixed in a 250-mL flask. The mixture was stirred at room temperature, followed by addition of excess of 1H,1H,2H,2H-perfluorooctylmethyldichrosilane($(CH_3)Cl_2Si(CH_2)_2(CF_2)_5CF_3$) (3.60 g, 7.8 mmol). The above mixture was stirred at room temperature for about 20 h, and then centrifuged at speed of 6000 rpm. The precipitates (silica particles) were washed ultrasonically with copious dichloromethane followed by repeated centrifugation. Finally, the fluoro-functionalized colloidal silica was preserved in methylisobutylketone at concentration of 13.7 wt.%, and readily used in further formulation. Other fluoro-functionalized colloidal silica with the sizes of 90-nm and 1450-nm were synthesized by the identical procedures.

Typical procedures for preparing methyl-functionalized colloid silica (340 nm) were described as follows. 101.0 g methyl-isobutylketone containing dispersed colloidal silica (concentration: 10.7 wt.%) were added to a 250-mL flask immersed into an oil bath at 95 °C. The mixture was flushed with argon for about 10 min, followed by addition of hexamethyldisilazane (12.1 g, 75.0 mmol). The above mixture was stirred for 3 h, and then centrifuged at speed of 8000 rpm when the mixture was cooled down to room temperature. The precipitates (silica particles) were washed ultrasonically with copious dichloromethane followed by repeated centrifugation. Finally, the methyl-functionalized colloidal silica was preserved in methylisobutylketone at concentration of 12.9 wt.%, and readily used in further formulation. Other methyl-functionalized colloidal silica with the sizes of 90-nm and 1450-nm were synthesized by the identical procedures.

2.4. Preparation of particle and binder based coatings

Functionalized colloidal silica were mixed with fluorocopolymer at volume ratios ranging from 1 to 85 vol.% by ultrasonication for 15 min, followed by magnetic stirring for additional 30 min. Designated amount of HDI (mass ratio: fluorocopolymer:HDI = 4:1) dissolved in cyclohexanone was added to the above mixture by magnetic stirring for about 10 min. The coating was prepared by spraying the mixture on clear glass slides (e-Tool® F-2 spray gun, air flow rate: 3 kg/cm²), followed by curing at 100 °C for 1 h.
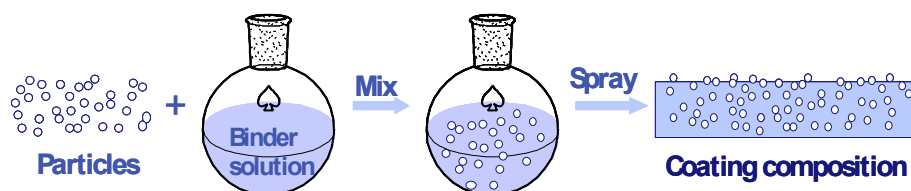

Fig. 1. Sketch of preparation process for particle and binder based coatings.