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Full Length Article

Texturing commercial epoxy with hierarchical and porous structure for robust superhydrophobic coatings

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ABSTRACT

The practical application of superhydrophobic coatings is restricted majorly by stability issues, especially in such cruel conditions as acid rain, pollutant contamination, and mechanical abrasion. In this work, we demonstrated a new type of superhydrophobic coatings with remarkable robustness and versatility using commercial epoxy as main building block. The hierarchical and porous structure was achieved by texturing micrometer-sized pores on the adhesive coatings, in which the SiO_2 nanoparticles were embedded. Due to strong substrate adhesion, excellent internal bonding, and micropore cushioning, the as-prepared superhydrophobic adhesive coatings can avoid the consumption of hierarchical structure after each abrasion and tightly anchor itself on substrate as well as soften the pressure during the mechanical force acting on them. The synergistic effect of these three protection mechanisms contributes to preferable mechanical robustness under severe sandpaper abrasions, cyclic tape peels, and knife scratches. This functional coating also can remain superhydrophobic after long-term exposure to a large variety of media, including corrosive solutions, daily consumed liquids, and water at different temperatures. Simultaneously, the epoxy resin has good compatibility with both hard and soft substrates, and thus providing such superhydrophobic adhesive coatings with high versatility for the applications in advanced functional materials. The concept of transforming commercial adhesive into superhydrophobic surface provides a simple and versatile approach to highly robust superhydrophobic materials.

1. Introduction

Superhydrophobicity, which is defined as a water contact angle (CA) higher than 150° and a sliding angle (SA) lower than 10°, is an evolutionary function for many natural creatures, e.g., it can be observed in water strider legs [1,2], rice leaves [3], butterfly wings [4], and lotus leaves [5,6]. Superhydrophobicity is achieved by exploiting hierarchical surface structures and low surface energy substances. Artificial superhydrophobic surfaces have attracted attention in a variety of fields, such as engineering, medical science, physics, and chemistry, because of their promise for self-cleaning [7–10], antifogging [11,12], anticorrosion [13,14], oil/water separation [15–18], and so on. In the past decades, diverse approaches have been created to achieve superhydrophobicity, including plasma treatment [19,20], self-assembly methods [21–23], vapor deposition method [24,25] and so on. For technical and practical purposes, superhydrophobic surfaces are prepared on various substrates, such as metal [26,27], lignocellulosic materials [28–31], glass [32,33], and sponges [34,35]. Their features have been studied systematically, such as wettability, morphology, application fields, and real-world performance. However, artificial superhydrophobic surfaces have low mechanical stability, which is a critical issue that affects practical applications. Therefore, there is a need to effectively enhance the mechanical robustness of superhydrophobic surfaces [36–39].

Three strategies can be used to address this issue. First, self-healing can be introduced to superhydrophobic surfaces by mimicking living things [40–44]. Once mechanical abrasions occurred, the damaged superhydrophobic surface can be healed by light irradiation, humidity, and so on. However, the high stimulus requirements make this strategy undesirable for realistic applications. Second, mechanical durability can be improved in a regenerative manner [45–47]. After the top layer is abraded away, the exposed surface still has hierarchical

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superhydrophobic structures. However, after the hierarchical structure has been exhausted completely, the superhydrophobicity would disappear. Third, the bonding strength can be enhanced by inserting reinforced coatings, such as adhesive layers, between superhydrophobic coatings and substrates [48,49]. This approach is considered the most promising approach among the three strategies. Nevertheless, such a sandwich-like structure is still weak because the superhydrophobic coating is deposited merely on the adhesive layer surface. Similar to the drawback of the second strategy, the superhydrophobic coating would be abraded away after multiple harsh abrasions. In this case, the medium adhesive layer is exposed and presents a smooth surface, which cannot provide the necessary roughness for superhydrophobicity.

Bearing the above consideration in mind, we reason that if the adhesive layer can be textured with hierarchical structures, then the resulting coating can serve as reinforce layer and provide superhydrophobicity simultaneously. In this way, the reinforced layer and the superhydrophobic layer are integrated into one coating. Such superhydrophobic coating not only has excellent bonding strength in its interior to avoid the consumption of hierarchical structures but also possesses strong substrate adhesion to tightly anchor itself on the substrates. Therefore, the coating can exhibit remarkable durability by using adhesives as the main building block.

In this study, we demonstrated the first example of a kind of superhydrophobic coatings by using commercial epoxy resin as the main building block. By texturing micropores on adhesive coatings that were embedded with SiO_2 NPs, micro/nano structures were achieved. Such kind of adhesive not only served as reinforced layer to boost mechanical durability but also provided a hierarchical structure to support superhydrophobicity. In particular, a large amount of microspores on the adhesive surface offered a cushion structure to soften the pressure during the mechanical force acting on them, which further enhance the robustness. This superhydrophobic epoxy resin adhesive can withstand various harsh abrasions without affecting its performance, including harsh sandpaper abrasions, cyclic tape-peels, and severe knife scratches. Interestingly, such coating also shows excellent resistance to liquid impalement into hierarchical structure after long time immersion at different media. Moreover, owing to the versatility of epoxy resin, the superhydrophobic adhesive can be glued to various substrates for robust functional surfaces.

2. Experimental section

2.1. Materials

Commercial epoxy resin adhesive (E-44) was provided by Yuanda Chemicals Co., Ltd. (China). SiO_2 nanoparticles (NPs) with diameters of 15 nm and 1H, 1H, 2H, 2H-perfluorooctyltrimethoxysilane (F13-TMS) were supplied by Aladdin Industrial Corporation (USA). Other chemical regents, including ethanol, hydrochloric acid, and sodium hydroxide, were purchased from Tianjin Damao Chemical Reagent Co., Ltd. (China). F13-TMS, SiO_2 NPs, and ethanol were used without further purification. Daily consumed liquids such as milk, red wine, and coffee were purchased from the local supermarket.

2.2. Preparation of superhydrophobic adhesive

The superhydrophobic adhesive was prepared by a thermally driven method previously reported by our team [50]. First, 1 g epoxy and 0.5 g curing agent were dispersed in ethanol under magnetic stirring. This was followed by the dispersion of SiO_2 and F13-TMS by ultrasonic oscillation for 1.5 h to obtain a reactant solution. The weight ratio among SiO_2, F13-TMS, epoxy, and ethanol was 1:0.5:1.5:50. The substrate, such as wood, metal, glass, cotton, or sponge, was placed into the bottom of the weighting bottle containing the reactant solution. The amount of reactants depended on the upper surface substrates (1 mL/cm^2). Thereafter, the bottle was incompletely sealed and heated at 110 °C. After 1.5 h, the superhydrophobic adhesive was coated on different substrates. To study the functions of all constituents in our formula, comparative coatings were prepared via the same method but with different reactants (Table S1, Electronic Supporting Information). Without a special statement, the superhydrophobic adhesive glued on wood was used to conduct characterizations and robustness tests.

2.3. Characterization

SEM images were collected on a Hitachi SU1510 electron microscope (accelerating voltage: 15 kV). Surface components and chemical structures were analyzed by EDS (Quorum K950X, UK) and FTIR spectroscopy (Shimadzu IRAffinity-1, Japan). Before conducting EDS and FTIR observation, all the test samples were washed using ethanol aiming to remove the unreacted F13-TMS. CAs (4 μL for all liquids) were collected using the OCA15 CA system provided by Dataphysics Instruments GmbH (Germany) at room temperature. SAs were obtained by calculating the CA hysteresis.

Sandpaper abrasion was conducted on the as-prepared coatings by using grit no. 800 sandpaper and a pressure of 5 kPa. The coatings were faced toward the abradant material and moved along one direction. The change in water CAs and SAs was measured every 10 cm of an abrasion length, which was defined as one cycle of abrasion. The resistance to liquid impalement was conducted by immersing the samples into different media for 6 h under magnetic stirring. The media include corrosive acid and alkali solution, daily consumed liquids (milk and coffee), and water at temperatures ranging from 0 °C to 95 °C.

3. Results and discussion

3.1. Characterizations of the as-prepared coatings

In this work, a formulation consisting of epoxy resin, SiO_2 NPs and F13-TMS was rationally designed to achieve hierarchical and superhydrophobic adhesive. To study the functions of all the constituents during the assembly of hierarchical epoxy resin, SiO_2 coating and SiO_2/F13- TMS coating were also prepared. SEM, EDS, CA, FTIR analysis were explored to characterize the morphology, element, wettability and functional groups of these coatings.

Fig. 1a shows that the SiO_2 coating was flat and did not have any concave or convex structures, thus indicating a relatively smooth surface. At a high magnification, the plane SiO_2 coating comprised dense SiO_2 NPs with diameters less than 50 nm (Fig. 1b). Demonstrated by the CA of 0° (Fig. 1c), this coating exhibited superhydrophilic wettability because of the numerous hydroxyl groups from SiO_2 NPs [51]. After the introduction of F13-TMS, some variations in morphology and wettability were observed. Some cracks were found on the SiO_2/F13-TMS coating, and roughness increased (Fig. 1d). Furthermore, the diameter of the SiO_2 NPs increased to ∼250 nm (Fig. 1e) because of the polymerization of F13-TMS, which agrees well with previous reports [29,52,53]. The random assembly of these hydrophobic SiO_2 NPs resulted in the rough SiO_2/F13-TMS coating and provided superhydrophobicity with a CA of 157° (insets of Fig. 1f). However, not all areas on the coating exhibited superhydrophobicity (Fig. 1f), indicating the hierarchical structure created by hydrophobic SiO_2 NPs was not consecutive. The low magnification of the SEM image further provided proof for the discontinuous superhydrophobicity. Some areas on the SiO_2/F13-TMS coating were still lacking in roughness even though protuberances and cracks were observed in other areas (Fig. 1d).

Superhydrophobicity was achieved on the whole surface by adding epoxy resin, as revealed by the spherical water droplets and CA values on the SiO_2/F13-TMS/epoxy coating (insets of Fig. 1i). Figs. 1g and S2 show that abundant microspores with diameters of ∼300 μm were created in the consecutive epoxy resin with thickness of ∼175 μm. Micrometer-sized pores were the result of impact force from gaseous ethanol [50]. Specifically, a large amount of ethanol was preserved