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Preparation of superhydrophobic polybenzoxazine/SiO_2 films with self-cleaning and ice delay properties

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ABSTRACT

Ice accumulation is a serious problem around the world, especially in cold regions. It is believed that a superhydrophobic surface has the potential to realize ice delay. Herein, we report an approach to fabricate superhydrophobic films combined with pendent aliphatic chain-substituted polybenzoxazine and silica nanoparticles (SiO_2 NPs) through spin coating and thermal curing. As a result, a superhydrophobic polybenzoxazine/SiO_2 film with a static water contact angle of 167 ± 2° and a water sliding angle of 5° was developed, which exhibits self-cleaning properties. The polybenzoxazine/SiO_2 film also exhibits ice delay properties owing to the decrease in the liquid-solid contact area and heat loss caused by air pockets under the micro-nano structure of the superhydrophobic film. Furthermore, the superhydrophobic polybenzoxazine/SiO_2 film retains its superhydrophobicity after heat treatment for 1 h within a wide temperature range. Moreover, the as-prepared superhydrophobic films are also stable over a wide pH range, from 1 to 14, or after UV exposure for 10 h.

1. Introduction

Ice accumulation in cold environments can have adverse impacts or even cause serious disasters in many areas such as aircrafts, off-shore oil platforms, power lines, wind turbines, marine vessels, and so on [1,2]. Currently, many anti-icing and de-icing technologies have been developed to prevent or reduce ice formation on these surfaces [3]. Superhydrophobic surfaces have attracted considerable interest for various applications owing to their special properties such as self-cleaning [4,5], anti-corrosion [6,7], anti-fogging [1,8], oil-water separation [9,10], and anti-icing [11,12]. Inspired by many plants and insects in nature, superhydrophobic surfaces with static water contact angle (WCA) greater than 150° have been developed [13–16]. As is well known, there are two keys to fabricate superhydrophobic surfaces: chemical modification of low surface energy materials, such as perfluorocarbon or fluoroalkylsilane [17] and roughening the surface morphology using complicated processes or multistep procedures such as sol-gel [18], chemical etching [19], electrodeposition [20], templating [21], and chemical vapor deposition [22]. Compared to these methods, spin coating is a convenient process for the fabrication of superhydrophobic films.

The anti-icing properties of superhydrophobic films have been reported in recent years [23–25]. Even though superhydrophobic surfaces undergo gradual mechanical damage during icing/de-icing cycles [26–28], they have numerous anti-icing applications, because of their low cost, low energy consumption, and simple structure [25]. Using the methods of soft replication and crystal growth, micropillar arrays of ZnO nanohairs have been prepared with a longest ice time of 9893s at −10 °C [29]. Guo et al. have reported that a long ice time can be achieved on micro/nanostructured surfaces prepared by ZnO nanohair planting and modification of heptadecafluorodecyltripropoxysilane (FAS-17) [30]. Besides, Nine et al. have reported that the ice time of superhydrophobic surfaces exhibiting “lotus effect” is longer than that of those exhibiting “petal effect” [31]. During these fabrication processes, construction of roughness on superhydrophobic films with anti-icing properties involves complicated processes or multistep procedures, such as etching, lithography, and so on. Hence, it is highly desired to design a low-cost and simple method to fabricate superhydrophobic films with self-cleaning and ice delay properties.

Although many superhydrophobic materials have been reported, fluoropolymers are widely used as low energy materials to prepare superhydrophobic films. However, fluoropolymers have potential health effects for human [32]; therefore, it is preferable to use non-fluorinated low surface energy materials to fabricate superhydrophobic films. As a new type of low surface energy material without fluorine atoms, polybenzoxazine is a competitive material for fabricating superhydrophobic films because of its good molecular design flexibility, high thermal stability, and low cost [33–35]. Until now, various

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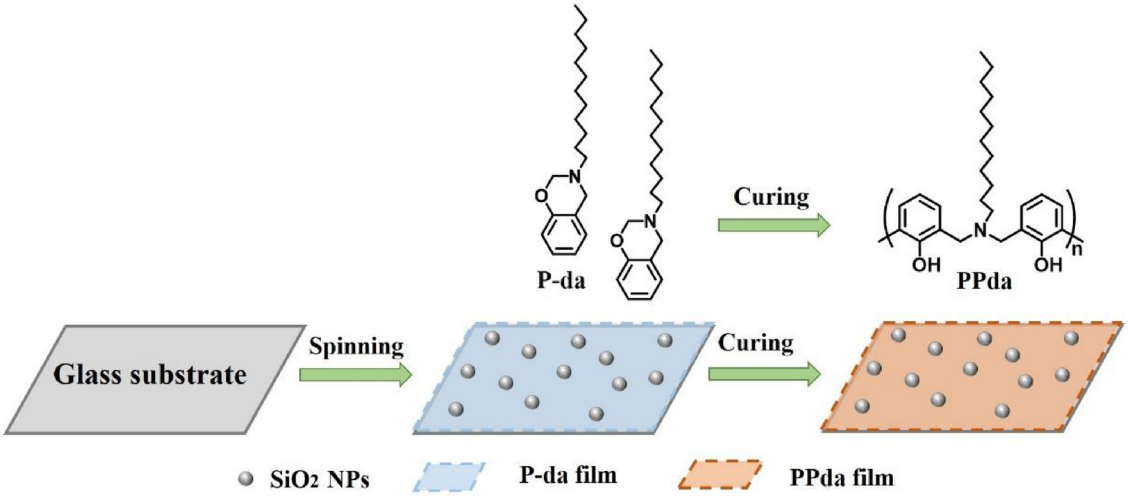

Scheme 1. Fabrication process of the superhydrophobic PPda/SiO_2 film on glass substrate.

superhydrophobic surfaces based on polybenzoxazine composites have been successfully developed. For example, Advincula et al. fabricated superhydrophobic and superoleophilic rubber-modified polybenzoxazine/SiO_2 nanocomposite coatings exhibiting "petal effect" superhydrophobicity and anti-icing property with a WCA of 158 ± 1° by dipping and spraying technique [36]. Liu et al. prepared a transparent "petal effect" superhydrophobic surface based on silane-functional polybenzoxazine with a highest WCA of 154.3° [37]. Raza et al. developed a superhydrophobic fluorinated polybenzoxazine-silica film with robust adhesion and dual pinning state using spray method [38,39]. Zhang et al. fabricated a fluorine-free superhydrophobic polybenzoxazine/TiO_2 surface with excellent thermal stability and self-cleaning property [40]. Hence, polybenzoxazine is an excellent choice of material to fabricate superhydrophobic films with self-cleaning and ice delay properties.

In our previous study, we reported that pendent aliphatic chain-substituted polybenzoxazine exerts a significant influence on the lotus effect performance [41]. Herein, we report the preparation of superhydrophobic polybenzoxazine (Poly(P-da), named as PPda) surfaces combined with silica nanoparticles (SiO_2 NPs) (named as PPda/SiO_2) by spin coating and thermal curing. The superhydrophobic surfaces possess self-cleaning and ice delay properties, high thermal stability, good UV-resistance, and excellent stability under different pH values. Furthermore, the ice time of the superhydrophobic polybenzoxazine surface was first measured quantitatively and then compared to that of an uncoated surface. The simple fabrication process and the excellent surface properties make this superhydrophobic surface suitable for industrial applications at various environmental conditions.

2. Materials and methods

2.1. Materials and chemicals

Aqueous formaldehyde solution (37%), phenol, and dodecylamine were purchased from Sinopharm Group Chemical Reagent Company. Ethanol, acetone, tetrahydrofuran (THF), chloroform, ethyl acetate, anhydrous sodium sulfate, hexane, hydrochloric acid, and sodium hydroxide were obtained from Shanghai Lingfeng Chemical Corp. All the chemicals were of analytical grade and used without any purification. Silica nanoparticles (size: approximately 20 nm) were purchased from Xianfeng Nanotechnology Company.

2.2. Synthesis of the benzoxazine monomer

The pendent aliphatic benzoxazine monomer was synthesized according to the method reported in the literature [42]. In a 250 mL three-neck flask, phenol (0.05 mol, 4.7 g) and aqueous formaldehyde solution (37%, 12.4 g) were mixed with chloroform (50 mL) under slight stirring, and then the system was heated to 65 °C. Then, dodecylamine (0.05 mol, 9.3 g) was added into the system under vigorous stirring and continued to react for 3 h. The crude products were dissolved in ethyl acetate and washed several times with aqueous NaOH (2 M) and water to remove unreacted materials. The solution was dried overnight and evaporated at room temperature to obtain the product. The product was purified by column chromatography to yield colorless transparent benzoxazine monomer (P-da) with hexane as the solvent. The synthesis procedures of P-da and its polymer are illustrated in Scheme S1. The chemical structure of P-da was confirmed by ^{1}H nuclear magnetic resistance (NMR) spectroscopy and Fourier transform infrared (FTIR) studies (see Figs. S1 and S2).

2.3. Preparation of PPda/SiO_2 coatings

Clean glass substrates (10 mm × 10 mm) were treated ultrasonically in deionized water, ethanol, and acetone for 5 min each. These substrates were then dried in an oven at 80 °C. The P-da benzoxazine monomer (0.1 g) was dissolved in 10 wt.% THF, and a certain amount of SiO_2 nanoparticles was added to the P-da solution. The mixed solution was sonicated and then spin-coated on a clean glass substrate at 1500 rpm for 40 s. Finally, the coated glass substrates were dried in a vacuum oven at 60 °C for 1 h to remove the solvent and then cured at 200 °C for 1 h. The fabrication process of the PPda/SiO_2 film on glass substrate is illustrated in Scheme 1.

2.4. Characterization

The chemical structures of the P-da monomer and the polymer were characterized by a Nicolet iS10 FTIR spectrometer at room temperature. The solution of P-da monomer was directly dropped on a KBr plate to form a thin film. The PPda film was formed after curing at 200 °C for 1 h. Moreover, ^{1}H NMR spectroscopy was performed using a German Bruker AVANCE III at a proton frequency of 400 MHz to characterize the chemical structure of the P-da monomer.

The wettability of PPda/SiO_2 coatings was characterized using a Dataphysics OCA 20 optical goniometer at room temperature. The static WCAs were measured using 4 μL deionized water droplets at an injection rate of 1 μL/s. When the static WCAs were greater than 130°, the contact angles were measured using the Laplace-Young method. On the other hand, when static WCAs were less than 130°, the Ellipse method was used to measure the contact angles. The water sliding angles (WSA)