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Building a mechanically stable polydimethylsiloxane/silica superhydrophobic coating on poly(chloro-p-xylylene) film by introducing a polydimethylsiloxane adhesive layer



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ABSTRACT

Building a superhydrophobic coating on polymer films is an important way to obtain water-proof surfaces. However, due to the poor mechanical strength and weak adhesion between coating and substrate, the superhydrophobicity of the coating is easily lost under mechanical loads. In this study, a facile approach was proposed to build a mechanically stable superhydrophobic poly(chloro-p-xylylene) (PPXC) film by pre-coating a polydimethylsiloxane adhesive layer (PDMS AL) on the original PPXC film and coating a superhydrophobic PDMS and silica (PDMS/SiO₂) layer on the PDMS AL layer. As demonstrated by Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) measurements, the thermal cross-linking reaction between the PDMS/SiO₂ coating and the PDMS AL layer could dramatically promote the interaction between the PDMS/SiO2 coating and the PPXC film. By tuning pre-curing time and the content of PDMS AL, the mechanical stability of the PDMS/ SiO₂ coating on PPXC film could be adjusted. Under the optimal conditions of pre-curing time and the content of PDMS AL, the PPXC film showed robust superhydrophobicity and self-cleaning ability against various mechanical damages, such as 3M tape peeling and cyclic abrasion. The superhydrophobic coating on PPXC film with PDMS AL showed a higher peeling resistance than that on PPXC film without PDMS AL. Moreover, the superhydrophobic coating on PPXC film with PDMS AL maintained its original superhydrophobicity even after 4000 cycles of abrasion.

1. Introduction

Electronic devices such as cell phones and telecommunication cabinets have been widely used outdoors. Therefore, it is necessary to improve the protection of the devices from electrochemical corrosion or electrical short circuits caused by moisture (water vapor) and liquid water. Poly(chloro-p-xylylene) (PPXC) film as a high moisture barrier material can be coated on various substrates by chemical vapor deposition (CVD) polymerization and has been used to protect semiconductor chips, sensors, and printing circuit boards [1-3]. Although the dense PPXC film can block moisture, it cannot effectively protect electronic devices from water-induced electrical short circuit due to its weak water repellency with a water contact angle (WCA) about 84°.

Besides, under high humidity, weak water repellency of the PPXC film also leads to its high adhesion with condensed water droplets, thus deteriorating the moisture barrier property of the PPXC film [4].

Droplets can easily roll away from a superantiwetting surface such as superoleophobic or superhydrophobic surface. Such surfaces usually have a high WCA greater than 150° and a low roll-off angle (RA) less than 10° [5–14]. The fabrication process of superhydrophobic surface is much easier and cheaper than that of superoleophobic surface because it is not required to use fluoride materials or special "Re-entrant" or "Overhang" structures to obtain the superhydrophobicity [15-17]. Therefore, endowing the PPXC film with the superhydrophobicity might be an effective strategy to improve the water repellency and solve the abovementioned problems [18]. Superhydrophobicity

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Fig. 1. Schematic diagram of the fabrication procedure of mechanically stable superhydrophobic coating on PPXC film controlled by introducing PDMS AL.

depends on chemical compositions with a low surface energy and proper micro- and nano-scale roughness [19-24]. Plasma etching is an important strategy to rough the materials for the purpose of obtaining superhydrophobicity [15,16,25]. For example, Bi and co-workers created a rough surface on PPXC film by plasma etching and adding the components with low surface energy [26,27]. The approach produced a superhydrophobic PPXC film, but it unavoidably damaged of the PPXC surface and probably degraded the water vapor barrier property of the film. Building a superhydrophobic coating consisting of a polymer binder and nanoparticles on the substrates was an alternative way to fabricate a superhydrophobic surface [28,29], which would not damage the underlying film [20,30,31]. In previous studies, superhydrophobic surfaces were obtained by spin coating, dip coating, spray coating or casting of silica (SiO₂) nanoparticles [32-34], but the superhydrophobicity of the coating prepared with these methods were easily destroyed under mechanical loads (e.g., peeling and abrasion tests) [35]. After complicated post-treatments, the mechanical stability of the coating could be greatly improved [36–40]. However, these multi-step treatments were not applicable to industrial fields. Recently, we fabricated stable superhydrophobic polydimethylsiloxane (PDMS) by onestep 3D printing [41]. However, this approach was characterized by the expensive cost and limited application scope. The weak stability of superhydrophobic coating with nanoparticles might be caused by its poor mechanical stability and weak adhesion strength between coating and substrates. In this case, pre-treatments might more efficiently improve the mechanical stability of superhydrophobicity than post-treatments. To enhance the adhesion between the superhydrophobic coating and the substrates, polar or reactive groups were inserted onto rigid substrates (e.g., glass and magnesium alloy) by pre-treatments [42-45]. Particularly, introducing an adhesive layer (AL) between substrate and coating could significantly improve the mechanical stability of the superhydrophobic coating by strong chemical bonding [46, 47]. To the best of our knowledge, fabricating robust superhydrophobic coating on the anti-stick plastic substrates such as PPXC film by introducing an AL was seldom reported. Besides, the effects of processing parameters of AL on the mechanical stability of the superhydrophobic coating were neglected.

Herein, we reported a facile and low-cost approach to fabricate a mechanically stable superhydrophobic coating based on PDMS and SiO₂ nanoparticles on PPXC film by inserting PDMS AL between the air plasma-treated PPXC film and the coating. The PDMS-wrapped SiO₂ nanoparticles were partially embedded in uncured PDMS AL in the cross-linking reaction during thermal curing. As a result, the superhydrophobic coating was robustly fixed onto the PPXC film by PDMS AL. By optimizing pre-curing time and the content of PDMS AL, the

fabricated superhydrophobic surface exhibited the excellent mechanical stability and could withstand both 3M tape peeling and more than 4000 cycles of abrasion tests without losing its superhydrophobicity and self-cleaning ability.

2. Experimental section

2.1. Materials

Poly(chloro-*p*-xylylene) (PPXC) film with a thickness of 110 μ m was provided by China Academy of Engineering Physics. Polydimethylsiloxane adhesive (PDMS, SE1700) and its curing agent (10:1 in weight ratio) were purchased from Dow Corning (USA). Hydrophobic SiO₂ nanoparticles (JT-SQ, 10–30 nm) were purchased from Chengdu Today Company (China). Alcohol and hexane were obtained from Kelong Chemical Company (Chengdu, China).

2.2. Building a PDMS AL on PPXC film

PDMS adhesive and its curing agent (10:1 in weight ratio) were dissolved in hexane to form an adhesive solution with various PDMS concentrations (0.0–6.0 wt%). Before dipping into the adhesive solution, the PPXC film was cleaned with alcohol and distilled water for three times (Fig. 1a) and treated with air plasma (Plasma generator, CTP-2000K, China) for 60 s under 150 V (Fig. 1b) to generate polar functional groups on its surface. Then, air plasma-treated PPXC film (denoted as PPXC-A) was dip-coated in the PDMS adhesive solution for 2 min with a dip coating machine (SYDC-100, Shanghai SAN-YAN Technology Co., Ltd., Shanghai, China) at a lowering speed of 6000 μ m/s and a lifting speed of 1000 μ m/s for 5 times. Finally, PDMS adhesive-coated PPXC film (denoted as PPXC-A/AL) was thermally pre-cured at 80 °C for 0–60 min (Fig. 1c).

2.3. Preparation of the superhydrophobic coating on PPXC-A/AL film

The PDMS adhesive with a curing agent (10:1 in weight ratio) was dissolved in hexane to form a homogeneous solution. Then, SiO_2 nanoparticles stabilized by PDMS were dispersed into the resultant solution and sonicated (100 W) for 30 min to obtain a homogeneous suspension. The weight ratio of PDMS to SiO_2 nanoparticles was set as 2:1 and the concentration of the final solution was 5.0 wt%. PPXC-A/AL film was dip-coated into the mixture solution of PDMS and SiO_2 nanoparticles, and then thermally cured at 80 °C for 60 min to form a robust superhydrophobic coating on PPXC film (denoted as PPXC-A/AL/AL/HL, Fig. 1d).

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