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Facile preparation of superhydrophobic surfaces with enhanced releasing negative air ions by a simple spraying method

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ABSTRACT

Superhydrophobic surfaces with micro/nano structures were prepared using the synergistic effect of the hydroxyl-silicone-oil modified microscale tourmaline particles (HTP) and the nanoscale silica (SiO_2) by a simple spraying method. The SiO_2/HTP/Polyurethane (PU) and HTP/PU dispersions were sprayed onto the waterborne polyurethane (WPU) film using a shower nozzle driven by an air compressor. After drying of the spraying film at room temperature, a surface with micro/nano structures was obtained and the micro/nano structures were consisted of the microscale HTP coated by the nanoscale SiO_2. Static water contact angle measurements proved that the rough surfaces were superhydrophobic. Furthermore, their performance of releasing negative air ion was significantly enhanced due to the rough structure. Importantly, this method is simple, low-cost and suitable for the fast and large-scale preparation of superhydrophobic surfaces, which is particularly important for the modification of hydrophilic polymer surfaces.

1. Introduction

Materials with superhydrophobic surfaces have recently received significant attention because of its importance in many biological processes and technological applications, which include self-cleaning surfaces, antifouling or foul-release coatings, stain resistant textiles, non-icing or ice repellant surfaces, etc. [1]. Two descriptions have been proposed for the dependence of the wetting behavior on surface roughness: the Wenzel and Cassie–Baxter models. The Wenzel model [2,3] holds for cases where the liquid remains in contact with the whole solid surface. The enhancement of hydrophobicity is quantitatively described by the Wenzel equation:

$$\cos\theta^{W} = r\cos\theta^{E} \tag{1}$$

where θ^{W} is the observed angle on the rough surface, θ^{E} is the equilibrium contact angle on the flat surface of the same chemical character, and r (with $r \geqslant 1$) is the ratio of the actual surface area to the projected area of the surface. This equation indicates that the surface roughness enhances the hydrophobicity of hydrophobic ones because r is always larger than 1.

The Cassie–Baxter model [4] holds for surfaces with a topography such that water cannot deeply penetrate and wet the whole surface, thus air is trapped into the grooves under the droplet, which is then suspended across the surface protrusions. In such a case, the droplet is in contact with a composite surface (solid and air) and the observed contact angle θ^{CB}, according to the Cassie–Baxter equation, is given by the linear combination:

$$\cos\theta^{CB} = f^{S}\cos\theta^{S} + f^{air}\cos\theta^{air} \tag{2}$$

By considering the air area fraction as $f^{air} = 1 - f^{S}$, $\theta^{air} = 180^{\circ}$, and assuming that the water contact angles of the solid fraction, θ^{S}, corresponds to that of the flat surface, θ^{E}, Eq. (2) can be rewritten as:

$$\cos\theta^{CB} = f^{S}\cos\theta^{E} + (1 - f^{S}) \tag{3}$$

Therefore, in this model, the hydrophobic character of a rough surface is enhanced by the decrease of the solid–liquid contact area [5].

According to the above theories, superhydrophobic surfaces have been prepared by a number of techniques including lithography [6], sol–gel processing [7], electrospinning [8], electrochemical methods [9] chemical vapor deposition [10] and others [1,11]. However, these methods are complex, time-consuming, expensive and not suitable for the fast and large-scale production in current stage. Recently, spray deposition, an alternative low-cost technique to rapidly coat a polymer solution on a variety of substrates to prepare polymer films, has been developed. Karapanagiotis et al. [12] prepared the superhydrophobic films by spraying hydrophilic

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silica (SiO_2)/poly(methyl methacrylate) (PMMA) suspensions and SiO_2/a commercial poly(alkyl siloxane) on glass surfaces. Bayer et al. [13] reported a superhydrophobic cellulose-based bionanocomposite fabricated by spraying a blend of cellulose nitrate and fluoroacrylic polymer dispersed in modified Pickering emulsions onto aluminum substrates. Zhu et al. [14] reported a superhydrophobic carbon nanotube film fabricated by one-step spray-coating method without any chemical modification on which the wettability can be reversibly switched between superhydrophobic and superhydrophilic by the alternation of UV irradiation and dark storage. Yilgor et al. [15] developed a multi-step spin-coating process that the dispersion of hydrophobic SiO_2 in tetrahydrofuran is coated onto a desired polymer surface to prepare polymer materials with superhydrophobic surfaces. However, the preparation of SiO_2 dispersions used in the coating process requires ultrasonic dispersion for 3 h at room temperature, requiring lots of energy and time. Srinivasan et al. [16] described a similar spraying technique to fabricate various microtextured surfaces from a polymer solution containing a perfluorinated dispersant, with the ability to control the morphology from fibers to beads-on-string and corpuscular structures. The incorporation of the low surface energy 1H, 1H, 2H, 2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane in the polymer solution confers these microtextured surfaces with significantly enhanced liquid-repellent properties.

In this article, superhydrophobic surfaces with micro/nano structures were prepared using the synergistic effect of the hydroxyl-silicone-oil modified microscale tourmaline particles (HTP) and the nanoscale SiO_2 by a simple spraying method. The SiO_2/HTP/Polyurethane (PU) and HTP/PU dispersions were sprayed onto the waterborne polyurethane (WPU) film to improve its hydrophobic properties. Furthermore, the performance of releasing negative ion was significantly enhanced due to the rough structure.

2. Material and methods

2.1. Materials

TP was purchased from Bao Hua Aion Powder Co., Ltd., Shenzhen, China. Hydrophobic SiO_2 HDK H2000 (H2K) was kindly provided by Wacker Chemie, Munich, Germany. Polytetramethylene glycol (PTMG, Mn = 2000), polycaprolactone glycol (PCL, Mn = 2000) and 4, 4-diphenyl methane diisocyanate (MDI) were supplied by An Li Artificial Leather Co., Ltd., Hefei, China. Petroleum ether, butanediol (BD), acetone, triethylamine (TEA), and butanediol (BD) and N, N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Hydroxyl silicone oil (HSO, C_{OH} = 280 mg KOH/g) was obtained from Foshan Vago Organic Silicon Co., Ltd., Guangzhou, China. Dimethylol propionic acid (DMPA) was obtained from Aladdin Reagent, Shanghai, China.

2.2. Modification of TP by grafting HSO

HSO and TP were heated at 100 °C under reduced pressure (5 Torr) for 6 h. Then, HSO and TP with the mass ratio of 1 to 1 were put into an autoclave and mixed by stirring. After mixing, they were sealed in the autoclave under nitrogen atmosphere and heated at 140 °C for 12 h. The treated TP was repeatedly washed using petroleum ether by vacuum filtration. The filtrate cake was placed in a vacuum oven at 90 °C for 12 h. At last, the dried cake was ground and sieved with a 200 mesh sieve to obtain the HSO-modified TP, which is designated as the HTP.

2.3. Preparation of WPU emulsions and WPU films

12.5 g of MDI, 20.0 g of PTMG, 20.0 g of PCL and 2.68 g of DMPA were put into a 500 ml three-necked flask equipped with a condenser tube, dropping funnel, and mechanical stirrer to react at 75 °C for about 3 h under nitrogen atmosphere. Then the NCO-terminated prepolymer was obtained. According to the NCO value determined by the standard dibutylamine titration method (HG/T 2409-92), a stoichiometric amount of BD dissolved in 40 ml acetone was added dropwise to extend the chain at 60 °C until the theoretical NCO content was reached. After that, the reaction mixture was cooled to 40 °C, and 2.1 g of TEA was added to neutralize the carboxylic groups of DMPA. After 30 min neutralization, distilled water was added to the mixture with vigorous stirring to obtain the WPU emulsion with the solid content of about 30 wt%. At last, the WPU emulsion was cast glass substrates and dried at 80 °C for 12 h to obtain the WPU films.

2.4. Preparation of HTP/PU and SiO_2/HTP/PU dispersions

A 500 ml three-necked flask equipped with a condenser tube, dropping funnel, and mechanical stirrer was charged with 10.0 g of MDI, 20.0 g of PTMG, 20.0 g of PCL and HTP at 75 °C. The mixture in the three-necked flask reacted at 75 °C for about 3 h with stirring to obtain the prepolymer. The temperature was then reduced to 60 °C, and a stoichiometric amount of BD dissolved in 60 ml DMF was added dropwise to extend the chain until the theoretical NCO content was reached. DMF was added in the process of expanding chain in order to reduce the viscosity of reaction system. At last, the 5 wt% HTP/PU dispersion with a solid content of about 30% was obtained, which was diluted in DMF to obtain the diluted HTP/PU dispersion with a solid content of about 10%. The 5 wt% TP/PU, 2 wt% SiO_2/5 wt% TP/PU and 2 wt% SiO_2/5 wt% HTP/PU dispersions were also prepared in the similar way.

2.5. Sample preparation by spraying

The spraying equipment is a shower nozzle driven by an air compressor, which is similar with Srinivasan's report. [16] The

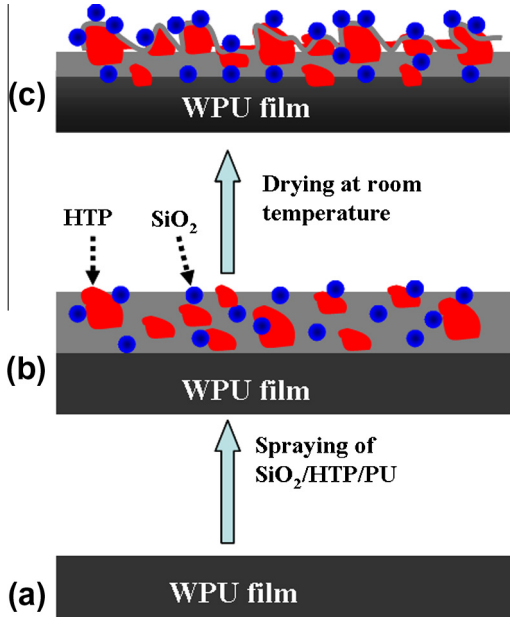

Fig. 1. Schematic of the preparation of superhydrophobic surfaces. (a) WPU film, (b) Spraying of SiO_2/HTP/PU dispersion, and (c) surfaces with micro/nano structures after drying.