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Superhydrophobic porous surface fabricated via phase separation between polyhedral oligomeric silsesquioxane-based block copolymer and polyethylene glycol

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ABSTRACT

A superhydrophobic porous film was fabricated by a simple phase separation process between a polyhedral oligomeric silsesquioxane (POSS) based diblock polymer (P) and polyethylene glycol (PEG) in selective solvents. The POSS-based hybrid diblock polymer was synthesized using a two-step atom transfer radical polymerization method. The polymer, along with PEG, was dissolved in mixed solvents of tetrahydrofuran (THF) and ethanol (AC), and then dip-coated onto the glass slides to form a coating film. After PEG was washed away using water, the polymer film with nano-micrometer dual-scale roughness on the slides was formed due to the phase separation. Then, a superhydrophobic porous film was obtained after surface modification with low surface energy material. The effects of POSS content, P/PEG ratio, and AC/THF ratio were investigated. The results showed that the water contact angle increased with the PEG content within a certain range and the surface roughness was enhanced after adding AC. When the POSS content was 25.3% (P2), the ratio of P2/PEG was 5:5 and AC/THF was 3:7, the film after modification had a static water contact angle of 155.1° and a sliding angle of 6.5°, demonstrating superhydrophobicity.

1. Introduction

Superhydrophobic surface is water-repellent with a static water contact angle exceeding 150° (WCA) and a sliding angle (SA) less than 10° [1]. Because of its potential applications in self-cleaning coatings [2–5], anti-corrosion [6–8], anti-icing [9–11], oil-water separation [12–15] and others [16–22], superhydrophobic surface preparation has attracted lots of interests. Nano-micrometer dual-scale roughness and low surface energy are the two key factors of a superhydrophobic surface according to the superhydrophobic mechanism of lotus leaves [23–25]. Many techniques have been developed to fabricate a superhydrophobic surface [26], such as sol-gel [27], chemical vapor deposition [28,29], spraying [30–32], lithography [33] and others [34], in which a rough surface was built firstly, then modified with low surface energy materials, for example, fluorinated copolymer [35], fatty acid [36] and fluorinated silane, etc. Inorganic nano-particles such as $CaCO_3$ [37], SiO_2 [32,37–40], ZnO [41], TiO_2 [42] and carbonnanotubes (CNTs) [43] are commonly used to create roughness.

Polymers in coatings are the main film-forming material. In recent years, polymers were solely used to construct surface roughness through phase separation of their own, thus to prepare superhydrophobic films, without inorganic nano-particles [44–46]. For instance, Tung et al. presented a superhydrophobic film with rough pincushion-like structure by employing the micro-phase separation of poly (vinylphenol)-*block*-polystyrene in different solvents [47]. Maruyama et al. prepared ordered mesoscopic honeycomb structures via casting the chloroform solution of amphiphilic polymers on solid surfaces at high atmospheric humidity [45]. In our previous work, the phase separation of polylactic acid/polyethylene oxide was used to construct roughness to prapare a superhydrophobic coating film [48]. However, the polylactic acid isn't a good film-forming polymer.

Polyhedral oligomeric silsesquioxane (POSS) has unique three-dimensional cage-like structures with a general size of 1–3 nm. Because of the big polarity difference between POSS parts and other organic parts in POSS-containing hybrid polymers, POSS parts are able to self-assemble into nano-sized aggregates and migrate onto the film surface. Inspired by this, POSS-containing polymers could be used to build rough surfaces. We prepared a superhydrophobic/superoleophilic

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cotton fabric by dip-coating cotton fabric in a POSS-containing polymer solution, in which a binary nano/micro roughness was achieved by combining nano-scaled roughness derived from phase separation of the POSS-containing polymer with the micro-scaled roughness on the fiber [49]. In addition, we synthesized the POSS-based fluorinated acrylate copolymer (MMA-BA-HEMA-FMA-MAPOSS) via free radical solution polymerization. By studying the surface roughness and wettability of the copolymer film, it was found that POSS would aggregate on the surface and formed nanoscale particles, leading to rough surface with great hydrophobicity [50].

In this paper, a rough superhydrophobic porous film was prepared using phase separation between polymers. A POSS-based hybrid diblock polymer with good film-forming performance was synthesized using a two-step atom transfer radical polymerization (ATRP) method. The polymer was mixed with polyethylene glycol (PEG) in selected solvents and then dip-coated onto glass slides. The phase separation between the polymer and PEG occurred during the solvent evaporation. Because of its water resolubility, the PEG was washed away from the film and a rough film was obtained. After modification with a low surface energy material, a superhydrophobic film was prepared. The effects of POSS content in the polymer P, P/PEG ratio, tetrahydrofuran (THF)/ethanol (AC) ratio, and the low-surface-energy modification on roughness and wettability were investigated. The transparency and the sand abrasion test of the superhydrophobic film were also reported.

2. Experiment

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA) and 2-hydroxyethyl methacrylate (HEMA) were washed twice with 5 wt% NaOH aqueous solution, then washed to be neutral with distilled water, dried with $CaCl_2$ over 48 h, and finally distilled under reduced pressure before use. Perfluoroalkylethyl methacrylate (FMA) was washed with 20 wt% NaOH aqueous solution several times until it was transparent, and then washed to be neutral with distilled water, dried over $CaCl_2$ and stored at 4 °C before use. Methacrylisobutyl polyhedral oligomeric silsesquioxane (MAPOSS) was recrystallized from methanol and dried in vacuum. 2,2-azobisisobutyronitrile (AIBN) was recrystallized twice from anhydrous ethanol. The catalyst, CuCl, was washed with glacial acetic acid and ethanol alternately until it was white, and then dried under vacuum at 50 °C for 12 h before use. The other reagents used in the experiments were all of analytical grade, in addition to PEG, chemically pure.

2.2. Synthesis of POSS-based hybrid acrylic block polymer

A two-step ATRP process was employed to prepare POSS-based hybrid diblock polymer (P(MMA-*co*-BA-*co*-HEMA)-*b*-PMAPOSS) according to the procedure shown in Scheme 1. Firstly, the macro-initiator (P(MMA-*co*-BA-*co*-HEMA)-Br) was synthesized as follows [51]. A mixture of MMA (3.50 g, 35 mmol), BA (5.47 g, 43 mmol), HEMA (1.82 g, 14 mmol), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) and solvent (cyclohexanone) was added to a 100 mL Schlenk flask equipped with a rubber septum and a stirring bar, and degassed by three freeze-pump-thaw cycles. Then CuCl (0.7 mmol) were added to the mixture. The system was again degassed by three freeze-pump-thaw cycles and sealed with a septum. The initiator (ethyl 2-bromopropionate) was then added. The flask was placed in an oil bath maintained at 70 °C for 16 h. The sample was diluted in THF and filtered through a small plug of Al_2O_3. Then the solvent was evaporated at room temperature. Secondly, a mixture of macroinitiator (2.8 g, 0.14 mmol), MAPOSS (0.5662 g, 0.6 mmol), PMDETA (0.05 g, 0.3 mmol) and solvent (methylbenzene) was added to a 50 mL Schlenk flask and the above steps were repeated. Wherein, the amount of CuCl was 0.0198 g (0.2 mmol), and the reaction was kept at 70 °C and stirred for 24 h. After reaction, the sample was diluted in THF and filtered through a small plug of Al_2O_3. Then under stirring, the solution was added into the mixture of methylalcohol and deionized water. The volume ratio of methylalcohol and deionized water was 3:1. The precipitate was collected and dried in vacuum at 35 °C for 48 h. At last, white solid marked as P1 was obtained. P2 (MAPOSS, 0.9435 g, 1.0 mmol) and P3 (MAPOSS, 1.887 g, 2.0 mmol) were prepared in the same way.

2.3. Preparation of superhydrophobic films

The procedure of the film fabrication is shown in Fig. 1. The POSS-based hybrid acrylic block polymer was dissolved with PEG in mixed solvent of THF and AC. The solution was dip-coated on glass slides. After dried naturally at room temperature, the slides covered with polymer films were immersed into deionized water for 4 h to remove water soluble PEG. After dried again at room temperature, the films on the glass slides were modified with a fluorinated acrylic polymer resin (MBHF) on the surface. The MBHF was synthesized by a typical free radical polymerization process according to our previous work [48]. The synthetic pathway is shown in Scheme 2. After dip-coated with 1 wt % solution of the MBHF in xylene and butylacetate, films on the slides became superhydrophobic.

2.4. Characterization

The Fourier transform infrared spectrometer (FTIR, PerkinElmer, USA) and Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) were used to determine the chemical compositions of MAPOSS, synthesized polymers at room temperature. The ^{1}H NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in $CDCl_3$ and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. An OCA 20 (Data Physics, Germany) was employed to measure the water contact angle and the sliding angle of the film with a water drop of around 4 μL applied to six different points for each film. The morphology of the surface was characterized by a scanning electron microscopy (SEM, Merlin, Germany) operated at 5 kV. Before examined using SEM, the sample was plated with gold for 7 min by the ion sputtering apparatus (Quorum, UK) in order to make the surface charge. Elemental analysis of the film surface was carried out by energy dispersive X-ray spectrometry (EDS, Bruker Nano GmbH, Germany) on SEM at 20 keV. The surface roughness was measured by atomic force microscope (AFM, Nanoscope IIIa Multimode, USA). The visible light transmission was investigated by UV–vis spectroscopy (3150 Spectrophotometer).

2.5. Acid-base method

van Oss et al. [52,53] deemed that the surface energy γ is composed of Lifshitz-van der Waals component γ^{LW} and Lewis acid-base component γ^{AB} that consists of a Lewis acid component γ^+ and a Lewis base component γ^-. Therefore, the surface energy for solid (*S*) or liquid (*L*) can be presented as Eq. (1) and Eq. (2), respectively.

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB} = \gamma_S^{LW} + 2\sqrt{\gamma_S^+\gamma_S^-}) \tag{1}$$

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB} = \gamma_L^{LW} + 2\sqrt{\gamma_L^+\gamma_L^-}) \tag{2}$$

Thus, the solid-liquid interface interaction energy γ_{SL} can be expressed as Eq. (3).

$$\gamma_{SL} = (\gamma_S^{LW} - \gamma_L^{LW})^2 + 2(\sqrt{\gamma_S^+\gamma_S^-} + \sqrt{\gamma_L^+\gamma_L^-} - \sqrt{\gamma_S^+\gamma_L^-} - \sqrt{\gamma_L^+\gamma_S^-}) \tag{3}$$

In combination with Eq. Young: $\gamma_S - \gamma_{SL} = \gamma_L \cos\theta$, the relationship between the surface energy components and the contact angle θ is obtained (Eq. (4)).

$$(\gamma_L^{LW} + 2\sqrt{\gamma_L^+\gamma_L^-})(1 + \cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_L^+\gamma_S^-}) \tag{4}$$