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Crosslinked superhydrophobic films fabricated by simply casting poly(methyl methacrylate-butyl acrylate-hydroxyethyl methacrylate)-b-poly(perfluorohexylethyl methacrylate) solution

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ABSTRACT

This study focuses on the preparation of superhydrophobic films by crosslinkable polymer material-Poly(methyl methacrylate-butyl acrylate-hydroxyethyl methacrylate)-b-Poly(perfluorohexylethyl methacrylate) (P (MMA-BA-HEMA)-b-PFMA) with a simple one-step casting process. Nanoscale micelle particles with core-shell structure was obtained by dissolving the polymer and curing agent in the mixture of acetone and 1H, 1H, 5H octafluoropentyl-1,1,2,2 tetrafluoroethyl ether (FHT). Superhydrophobic films were fabricated by casting the micelle solution on the glass slides. By controlling the polymer concentration and acetone/FHT volume ratio, superhydrophobic polymer film with water contact angle of $153.2 \pm 2.1^{\circ}$ and sliding angle of 4° was obtained. By introducing a curing agent into the micelle solution, mechanical properties of the films can be improved. The adhension grade and hardness of the crosslinked superhydrophobic films reached 2 grade and 3H, respectively. The hydrophobicity is attributed to the synergistic effect of micro–submicro–nano-meter scale roughness by nanoscale micelle particles and low surface energy of fluoropolymer. This procedure makes it possible for widespread applications of superhydrophobic film due to its simplicity and practicability.

1. Introduction

Superhydrophobic surfaces, defined as surfaces with a water contact angle (WCA) larger than 150° and low contact angle hysteresis, have attracted considerable attentions in recent years [1]. This type of surface has been widely used in applications including antifogging, self-cleaning, anticorrosion, water harvesting, etc. [2–4]. It has been revealed that a peculiar topology based on micro- and nanoscopic surface roughness combined with the hydrophobic properties of its epicuticular wax is a prerequisite for superhydrophobic film [5]. Considerable efforts have been focused on the development of superhydrophobic surfaces through the design of proper roughness. Various approaches, based on sol–gel [5–8], the sublimation of aluminum acetylacetonate [9], lithography [10], spinning [11], chemical etching [12] and others [13–15] were reported.

Among these methods, polymer film casting, such as fluorinated copolymer [16] and polystyrene [11], have been proved to be a scalable methodology. For example, block copolymer were used to prepared superhydrophobic films through phase separation to form surface with variable morphology [17]. Xie et al. prepared a superhydrophobic surface by casting a micelle solution of the diblock copolymer of polypropylene-b-poly(methyl methacrylate), under an ambient atmosphere [18,19]. Deepak and Asha revealed that a polymer possessing both bulky units and polar structures as side chains could self-organize when a certain amount of water was added to the polymer solution for phase separation [20]. In our previous study, a block copolymer-poly(methyl methacrylate-butyl methacrylate-hydroxyethyl methacrylate)-b-Poly(perfluorohexylethyl methacrylate) (P (MMA-BMA-HEMA)-b-PFMA) was used to fabricate hydrophobic surfaces [21]. However, major challenge remains in developing scalable methodologies that enable superhydrophobic coatings on versatile substrates with a combination of strong mechanical and chemical stability, etc. [22].

In this paper, we prepared a crosslinked superhydrophobic surface with good mechanical performance. A fluorinated block copolymer, poly(methyl methacrylate-butyl

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acrylate-hydroxyethyl methacrylate)-b-poly(perfluorohexylethyl methacrylate) (P(MMA-BA-HEMA)-b-PFMA) was synthesized using a typical ATRP method. By mixing this copolymer in acetone and 1H, 1H, 5H octafluoropentyl-1,1,2,2-tetrafluoroethyl ether (FHT), micelles with core-shell structure was obtained. The micelle was cast onto clean glass to prepare superhydrophobic film by self-assembly of the fluorinated block copolymer. Curing agent of tolulene diisocyanate (L75) was introduced into micelle solution to improve the adhesion and hardness of film through crosslinking reaction between hydroxyl groups of the fluorinated block copolymer and -NCO groups of L75. The superhydrophobic films improve mechanical performance that satisfies practical application (e.g. self-cleaning) and have good potential application prospects.

2. Experimental

2.1. Synthesis of the fluorinated block copolymer

P(MMA-BA-HEMA)-b-PFMA was obtained from macro-initiator (P(MMA-BA-HEMA)-Br) and FMA according to the procedure outlined in Scheme 1. Firstly, a typical ATRP was carried out as follows. A mixture of MMA (2.00 g, 20 mmol), BA (10.14 g, 30 mmol), HEMA (1.3 g, 10 mmol), ligand (PMDETA) and solvent (xylene, dimethylformamide (DMF) or cyclohexanone) was added to a 50 mL Schlenk flask equipped with a rubber septum and a stirring bar, and degassed by three freeze–pump–thaw cycles. Then CuCl (0.3 mmol) and $CuCl_2$ (if necessary) were added to the mixture. The system was again degassed by three freeze–pump–thaw cycles and sealed with a septum. The initiator (EBiB or EBP) was then added. The flask was placed in an oil bath maintained at the desired temperature [23]. The sample was diluted in acetone and filtered through a small plug of Al_2O_3. Then the solvent was evaporated at room temperature. Secondly, a mixture of macroinitiator (2 g, ≈0.1 mmol), FMA (2.1 g, ≈4 mmol), ligand (PMDETA) and solvent (cyclohexanone) was added to a 50 mL Schlenk flask equipped with a rubber septum and a stirring bar. After repeating the above steps, the product, P(MMA-BA-HEMA)-FMA, was prepared.

2.2. Preparation of superhydrophobic surfaces

P(MMA-BA-HEMA)-b-PFMA (0.04 g) was dissolved slowly in 0.015 mL acetone under ultrasonic environment. Then the mixture was admixed in succession with 0.04 g L75 and 0.7 mL FHT, and was sonicated to accelerate the dissolution. The solution was directly cast-coated on a clean tin surface and then dried in an ambient environment.

2.3. Characterization

Shape and size of micelle particles were measured by transmission electron microscopy (TEM) (JEM-100CXII). The morphologies of the films were examined by scanning electron microscope (SEM) supplied by LEO (LEO 1530VP). An atomic force microscopy (AFM) (Dimension CSPM2000) was used to investigate the topography of thin film on glass. Images were acquired under ambient conditions in tapping mode using a Nanoprobe cantilever. Contact angle for water (WCA) and slide angle (SA) were measured with an OCA15 contact angle goniometer (Dataphysics Co., Germany). Each WCA and SA value was averaged from five measurements made at different positions of the film surface.

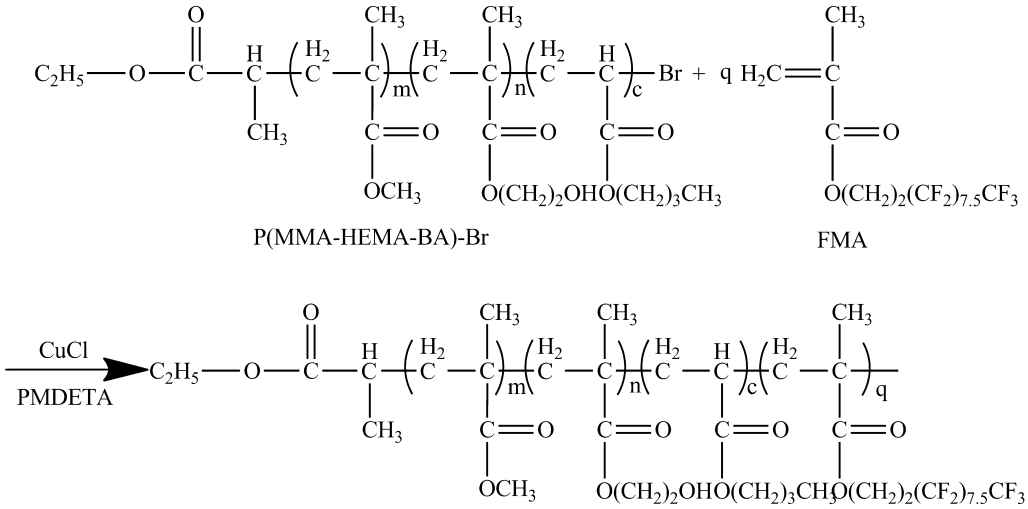
2.4. Test method of basic performances of superhydrophobic film

Analysis of adhesion grade was conducted according to adhesive attraction test methods in GB/T9286-1998 [14,15]. According to this standard, the blade is used to cut the film to make a lattice pattern on the film, with the number of both horizontal and vertical cuts being 6 in every cutting graph. The result is grade 0 when the cut line is smooth and no lattice drops off. The test was executed at least three times on one sample.

Hardness of the film was also examined with the pencils of different hardness going substantially parallel to the major axes of the test specimen. We carried out the experiment according to the Chinese national standard of GBT 6739-2006.

3. Results and discussion

The synthetic route of the copolymers is shown in Scheme 1. Chemical structures of the final products were verified by FTIR (Fig. 1) and ^{1}H NMR (Fig. 2). Fig. 1(a) shows the characteristic absorption peak located at 1446 cm^{-1} represents the CH_3 group in MMA [24]. The peaks at 2932 cm^{-1} and 2854 cm^{-1} are due to stretching vibration of $-CH_3$ and $-CH_2$ in HEMA, BA and FMA. The appearance of a wide absorption at 3435 cm^{-1} is stretching



Scheme 1. The procedure for preparing fluorinated block copolymer.