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Preparation of breathable and superhydrophobic coating film via spray coating in combination with vapor-induced phase separation

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ABSTRACT

Breathable and superhydrophobic coating film has been successfully prepared in one step by combining spraying technique and non-solvent vapor induced phase separation. Namely, solution of an inexpensive commercially available thermoplastic elastomer, i.e., a star-shaped triblock copolymer of poly (styrene-*block*-butadiene- *block*-styrene), was sprayed in an ethanol vapor atmosphere. The sprayed tiny droplets of the polymer solution facilitated the solvent evaporation and the non-solvent condensation, resulting in their fast phase separation and solidification. After complete evaporation of the solvent in a few minutes, a porous and superhydrophobic coating film was thus obtained, with a nanometer to micrometer interconnected nodular morphology. In order to improve the superhydrophobicity and strengthen the coating film, inorganic nanoparticles of SiO_2 have been added into the polymer solution for spraying fabrication. The obtained coating films were thermally treated to further improve their mechanical properties for practical application. The contact angle, the sliding angle and the abrasion tests results proved all previous methods effective. Moreover, water-vapor permeation through the coating film was checked to indicate its breath ability. Therefore, this paper provides a practical method for the preparation of porous and superhydrophobic coating films, which may have great promise in microfiltration and textile industry.

1. Introduction

Superhydrophobic surfaces with a water contact angle greater than 150° have been attracting more and more attention in recent years [1–3]. Many attempts have been made to mimic water-repellent biomaterials from nature, such as lotus leaves [4], water strider legs [5] and cicada wings [6] to fabricate superhydrophobic materials. Up to now, many techniques have been developed for that purpose, including electrospinning [7,8], spray-coating [9–11], sol-gel process [12], lithography [13], electrochemical deposition [14], layer-by-layer process [15], solution-immersion method [16], chemical vapor deposition [17] and plasma technique [18]. However, the high price of low-surface-energy materials and/or strict preparation conditions of superhydrophobic surface, is limiting the applications of this kind of materials. Therefore, it remains a challenging task to find a practical and economical way to fabricate superhydrophobic surface for practical applications.

In our previous work [19], a linear triblock copolymer of poly(styrene-*block*-butadiene-*block*-styrene) was dissolved in a selective solvent of methyl-ethyl ketone to form a micelle solution, which was then casted onto the substrate in an ethanol vapor atmosphere. After solvent evaporated naturally, a porous film was obtained to show superhydrophobic property, which was attributed to its rough surface with a pearl-necklace-like morphology. The micelle state of the block copolymer in solution was considered to accelerate the phase separation of the polymer solution during preparation, which is critical to the formation of the pearl-necklace-like morphology. The preparation is a vapor induced phase separation (VIPS) process, a technique for the preparation of porous materials especially porous membranes [20]. VIPS is a process to cast the polymer solution in an atmosphere of non-solvent vapor (usually water). Solvent evaporation cools the polymer solution surface and leads normally to the condensation of non-solvent in the atmosphere. As a result, phase separation takes place with the heat and mass transfer of the system, so that a porous structure will be formed from the separated phases after the complete evaporation of solvent. Lately, VIPS has been applied for the fabrication of superhydrophobic surfaces with specific surface morphologies [20–24]. For example, Xu et al. [21] casted the polycarbonate solution in humid air to prepare a superhydrophobic surface, which has a flower-like morphology and nanometer to micrometer scaled hierarchical microstructure.

It has been found that spherical polymer particles would be formed when the cast polymer solution evaporated the solvent in

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an organic non-solvent vapor atmosphere [19,25–27]. The organic non-solvent vapor in the atmosphere will condense and diffuse into the polymer solution, resulting in phase separation, which is similar to the usual VIPS process employing water vapor. However, the preparation is a dynamic process, and the final morphology and the scale of the formed polymer particles are associated with the volatilities of solvent and non-solvent, their condensation enthalpy, and their diffusion into each other.

In this work, the VIPS process and the spray-coating technique have been combined in order to prepare a porous coating film with superhydrophobic property. An inexpensive commercially available thermoplastic elastomer of a star-shaped triblock copolymer of poly(styrene-*block*-butadiene-*block*-styrene) was dissolved in tetrahydrofuran, and was sprayed onto the substrate using an air-spray-gun in an ethanol vapor atmosphere. The sprayed tiny droplets of the polymer solution would facilitate the mass and thermal transportation to accelerate solvent evaporation and non-solvent condensation. Therefore, phase separation of the sprayed polymer solution droplets was anticipated to take place quickly, and their solidification would emerge rapidly to form the porous coating film with a rough surface. Meanwhile, the spray-coating technique has the advantages such as easily handling, convenient for large-scale preparation and practical for non-planar-coating [28]. Moreover, hydrophobic SiO_2 nanoparticles have been added into the polymer solution for the spraying fabrication, because the inexpensive SiO_2 could efficiently increase the surface roughness to improve the superhydrophobicity and strengthen the coating film [29]. The coating film was thermally treated to further improve its mechanical properties. Water repellency of the coating film and the water-vapor permeation through the film have been checked to indicate its potential applications.

2. Experimental section

2.1. Materials

The star-shaped four-arm poly(styrene-*block*-butadiene-*block*-styrene) [Lot#4402, coded as (SB)4 in the context] was anionically polymerized, and its weight-average molecular weights (M_w) was measured by light scattering to be 220 kg/mol, polydispersity index (d, $d = M_w/M_n$, M_n is the number-average molecular weight) to be 1.11 by GPC, and butadiene content to be 74.4% through ^{1}H NMR measurement [30]. Analytical grade sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH), isopropanol and acetone were purchased from commercial resources in China and used without further purification. Hydrophobically modified fumed silica nanoparticles (HMFS, Aerosil R-812) were purchased from Evonik Industries, Germany. Plain weave polyethylene terephthalate (PET) fabric (192.5 g/m^2) was purchased from a local market. Deionized water was used throughout.

2.2. Preparations

The preparations were carried out in a sealed glove box, in which water vapor was removed by allochroic silicagel dehydrant to reach a relative humidity of less than 45% in the glove box. Sufficient non-solvent such as liquid EtOH stored in a beaker was positioned in the glove box for 24 h in advance, in order to maintain a saturated non-solvent vapor atmosphere. A commercial air spray gun (Morita spray gun, F-3, Auarita, Taizhou, China) was employed for the coating film preparation. The working pressure of the spray gun was 0.6 MPa, and the distance between the spray gun and the substrate was 15 cm in all the preparations.

Desired amount of HMFS nanoparticles were dispersed in 15 mL THF after vigorous sonication for 1 h, then 450 mg of block copolymer of (SB)4 was added and stirred vigorously to obtain an even mixture slurry. The obtained slurry was loaded in the spray gun, and was sprayed onto the substrate in the glove box full of saturated non-solvent vapor at room temperature. In each preparation, 15 mL of the feed solution was vertically sprayed on a clean glass substrate or PET fabric with an area about 7.5×7.5 cm^2. A solid white coating on the glass substrate or the fabric was obtained after solvent evaporation within 10 min. Through the process, the obtained coating films have mass ratios of (SB)4 to HMFS of 15:0, 15:1, 15:2, 15:3 and 15:4, respectively.

2.3. Characterizations and measurements

The film coatings were sputter-coated with a thin layer of platinum nanoparticles and then observed with a field emission scanning electron microscope (FE-SEM, SU-70 scanning electron microscope, Hitachi, Japan).

The wetting behavior of those coating films was measured with an FM40Mk2 contact angle meter (EasyDrop, KRUSS GmbH, Germany) under ambient condition. Five microliter water was carefully dropped onto the coating surface to measure its contact angle (CA, °). Water sliding angle (SA,°) on the coating film was measured according to the reference method [31]. Five independent measurements on different parts of the same coating were averaged to give its contact angle and sliding angle values, respectively.

The coatings were immersed in aqueous buffers with pH of 1 and 14 separately for 12 h, and then the contact angles of water droplet on those treated coatings were measured after drying them under ambient condition for 24 h. The chemical stability and corrosion resistance of the coatings were evaluated by comparing the contact angles before treatments and those of after.

The prepared coating films were treated at 110 °C in an electrical oven for 1 h in order to improve its abrasion resistance, which were checked with a sandpaper-abrasion method according to the literature [32]. The thermally treated coating film on a glass substrate (2.5×2.5 cm^2) was placed face-down to the sandpaper, and then the coating film surface was longitudinally and transversely (10 cm for each direction) abraded by the sandpaper under a weight at 100 g, respectively, which was defined as 1 cycle. Water contact angles for the abraded coating surfaces were measured after each 5 cycles' test.

The coating sprayed on PET fabric was used to seal a glass bottle filled with water. After stored in an air-dry oven at 45 °C for 48 h, the amount of evaporated water was measured, and was compared with that of by the untreated PET fabric to evaluate its water-vapor permeability.

3. Results and discussion

3.1. Pure polymer coating film

VIPS is known as a procedure of casting polymer solution in an atmosphere of non-solvent vapor (usually water vapor). During the process, solvent evaporation will result in cooling of the surface of the cast polymer solution, which leads to the condensation of the non-solvent vapor in the atmosphere. If the non-solvent is immiscible with the solvent, the condensed liquid will normally template the polymer solution surface to leave ordered holes after complete evaporation of the solvent, which is known as the breath figure process [26,27]. When the condensed non-solvent is miscible with the solvent, their mixing would normally result in phase separation of the polymer-containing system, which leads to the generation of the porous microstructure of the surface of the final material after