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# Preparation of superhydrophobic porous coating film with the matrix covered with polydimethylsiloxane for oil/water separation

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ABSTRACT

In this work, an organic coating film was designed to have a porous microstructure together with a rough surface, and its matrix was covered with a low surface energy layer, so that it can be employed for oil/water separation based on its superhydrophobicity and superoleophilicity. First, a mixture solution of poly(styrene-*block*-butadiene-*block*-styrene) (SBS) and polydimethylsiloxane (PDMS) prepolymer was sprayed onto stainless steel mesh in a non-solvent vapor atmosphere of ethanol. After solvent evaporation, a porous coating film has been obtained. The film matrix was formed from SBS to have a nodular-microstructure, which was covered by the highly flexible PDMS prepolymer. Then, the PDMS prepolymer was cured to cover the nodular microstructure at 60 °C, which was chosen to be far below the glass transition temperature of polystyrene block of SBS in order to maintain the formed nodular microstructure. The microstructures of the obtained coating films were carefully characterized and analyzed. Water and oil contact angles on the coating films were measured to indicate their wetting properties of superhydrophobicity and superoleophilicity. The oil diffusion speed along the coating film and the oil swelling behavior were examined to suggest the advantages of the covering PDMS layer. The coating films have been employed for oil/water separation through self gravity-driven filtration, where oil could penetrate the coating film automatically while water retained. The oil separation rate was found to be higher than 99.0% and the flux was estimated to be greater than 162 $L{\cdot}h^{-1}\,m^{-2}$. Moreover, the cycling tests suggest the satisfactory reusability of the coating film, implying its potential applications in oily wastewater treatment or oil spill recovery.

## 1. Introduction

Social life of human sometimes causes severe environmental problems such as oil spills and industrial organic pollution. To recover oil and to separate oil-and-water mixture will not only save energy, but also protect environment, which contributes to the tremendous demands for the worldwide sustainable development [1,2]. Several strategies have been established to clean oil spill such as skimmers [3], *in situ* burning [4] and chemical dispersants [5]. However, those methods are relatively inefficient and expensive, and in some cases cause secondary pollution. Lately, materials with specific wetting properties to water or to oil have been intensively tested to separate oil-and-water mixture, and is hoped to overcome the drawbacks of the traditional methods [2,6,7]. Those materials could be either inorganic or organic, and they usually have particular microstructures to allow oil penetrate but repel water, or the inverse. Specific nanofabrication technologies are often required to obtain the inorganic materials for that purpose. In comparison, the organic materials have the advantages such as easily processing, high elasticity and satisfactory durability, and have attracted more and more attention for the treatment of oily water.

The organic materials with hydrophobic and oleophilic properties have been fabricated into powder [7] or three dimensional porous sponges [7–11] to selectively absorb oil, and the absorbed oil could thereafter be released by squeezing. Moreover, they can be prepared either into porous flat films [12–16] or coated onto mesh substrates [1,17–24]. For examples, Su et al. [23,24] developed a strategy combining dip-coating and curing to fabricate organic based nanocomposite coatings on textile mesh, which show fantastic surface properties such as superhydrophobicity and superoleophilicity. The materials with those surface properties can realize separation of oil and water through filtration, which is driven by self gravity of oil or water [2,6,7,23,24]. The self gravity-driven filtration would thus greatly facilitate the massive treatment of oily water, based on the fact of huge amount of oil-polluted water in normal case. The films or the coatings are mainly prepared from low surface energy materials such as fluorine compounds and silane based polymers, the former of which suffer from the high

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price while the latter from the insufficient water repellency (relatively low water contact angle) [25].

Lately, we employed vapor induced phase separation (VIPS) method to have successfully prepared organic coating films with superhydrophobicity [26,27]. By casting polymer solution in non-solvent vapor atmosphere, the solvent evaporation cooling will result in condensation of the non-solvent vapor in the atmosphere onto the polymer solution surface, which leads to formation of porous coating film with rough surface. In addition, the VIPS process was further combined with spray technique to prepare a breathable coating film with superhydrophobicity [28]. The spray-coating technique has the advantages such as easily handling, convenient for large-scale preparation and practical for non-planar-coating [22,28–31].

In this work, a coating film with both superhydrophobicity and superoleophilicity was designed, and was prepared by the above mentioned strategy of combining spray technique with the VIPS process in one step. First, mixture solution of poly(styrene-*block*-butadiene-*block*-styrene) (SBS) triblock copolymer and polydimethylsiloxane (PDMS) prepolymer was sprayed onto stainless steel mesh in non-solvent vapor atmosphere of ethanol. During the VIPS process, the block copolymer of SBS would form porous and rough matrix of film, while the PDMS prepolymer was anticipated to cover the matrix but not to block the pores, based on its high flexibility [25,32]. The PDMS prepolymer was thereafter cured under an elevated temperature, which was below the glass transition temperature of SBS to maintain the formed nodular microstructure. In this manner, a composite coating film could be thus obtained to have the SBS matrix covered with the cross-linked PDMS. It is worth mentioning that PDMS is a well known organic coating material based on its excellent physiochemical properties such as flexibility, high thermal stability and chemical resistance [23–25,32]. Therefore, the composite coating film would combine the advantages of the covering layer of PDMS and the rough and porous SBS matrix. The microstructures and the wetting behaviors of the obtained coating films were carefully examined and analyzed. Moreover, the coating films were used to separate oil/water mixture through gravity-driven filtration, and their cyclic performances were checked and evaluated. Our results indicate that the coating film on the strong support of the stainless steel mesh may have promising applications in oily wastewater treatment or oil spill accident to recover oil.

## 2. Experimental section

### 2.1. Materials

Star-shaped four-arm poly(styrene-*block*-butadiene-*block*-styrene) (Lot#4402, coded as SBS 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 [33]. Polydimethylsiloxane (PDMS) prepolymer (Sylgard 184 A) and the curing agent (Sylgard 184B) were purchased from Dow Corning Corporation. Dodecane (98% purity) was purchased from Aladdin Industrial Corporation, China. Analytical grade ethanol (EtOH), tetrahydrofuran (THF) and acetone were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). All reagents were used without further purification. Stainless steel meshes with pore size about 37 μm were purchased from a local market. Deionized water was used throughout.

### 2.2. Preparations

The PDMS prepolymer and the curing agent with their mass ratio of 10:1 were dissolved in THF, and the block copolymer SBS was dissolved in THF too. Then the solutions were mixed to obtain homogeneous mixture solution, which had total solid mass content of 10% and the desired mass ratios of SBS to PDMS.

Preparation of the coating film was carried out in a glove box, in which water vapor was removed by dehydrant of allochroic silicagel to reach a relative humidity less than 45%. Sufficient non-solvent of liquid EtOH was stored in a beaker in the glove box for 24 h in advance 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 each preparation, 20 mL of the above prepared mixture solution was vertically spun onto glass slide substrate or stainless steel mesh. A solid white coating on substrate was obtained within 10 min. The sprayed coating films were then dried in air at room temperature for another 2 h to evaporate remaining solvents completely, and then cured at 60℃ for 12 h. The coating films sprayed on the glass substrate could be easily peeled off for characterizations and measurements, while the coating films were attached to the stainless steel mesh firmly, as described in our former work [28]. Through the procedure, the coating films with mass ratios of SBS to PDMS of 30:0, 30:10, 30:20 and 30:30, have been successfully prepared, 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, Hitachi, Japan).

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the surfaces of the coating films were recorded using a Nicolet AVATAR 360 spectrometer (Nicolet, USA) equipped with a Nicolet OMNI-Sampler ATR Smart Accessory (Ge, DTGS). The samples were vacuum dried at 40 °C for over 48 h before measurements, and were scanned at a step of 4 $cm^{-1}$ within the range of 4000 $cm^{-1}$ to 525 $cm^{-1}$.

The wetting behavior of the coating films was measured with a contact angle measuring system (EasyDrop, Krüss GmbH, Germany) under ambient condition. Five microliter water or dodecane was carefully dropped onto a film surface to measure its contact angle (CA, °). Five independent measurements on different parts of a same coating film were averaged to give its contact angle.

The prepared coating film with mass $M_1$ was immersed in dodecane for 24 h. Then it was taken out, and the dodecane on the surface was quickly removed by filter paper to weigh its mass $M_2$. The swelling rate (*SR*, %) was calculated according to three specimens of each coating film were tested in parallel to obtain an average *SR*.

$$SR = (M_2 - M_1)/M_1 \times 100\% \quad (1)$$

The coating film sprayed on stainless steel mesh was cut into 5 × 1 cm slice and vertically hanged, and the bottom end was positioned to just contact with dodecane, which was stored in a Petri dish. The oil diffusion in the coating film was measured by the height of the diffused level of the red dyed dodecane, as schematically illustrated in Fig. 1A. The diffusion distance within 5 min was recorded, and three independent measurements were averaged for each coating film.

The oil/water separation was performed on a filtration device, as shown in Fig. 1B, where the filter paper was replaced with the coating film on stainless steel mesh (51.2 mm in diameter). The device was tilted about 30°. After pouring the mixture of oil (dodecane) and water into the upper container, the separation would start. For clearer observation, the used water and oil were dyed by methyl blue and Oil Red-O, respectively. An optical microscope with a camera accessory (OM, ME600, Nikon, Japan) was employed to observe the separated oil phase and the water phase to evaluate the separation efficiency.

## 3. Results and discussion

The stainless steel mesh substrate has an average pore size about