Journal of Colloid and Interface Science 511 (2018) 21–26

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Short Communication

One-step preparation of superhydrophobic acrylonitrile-butadiene-styrene copolymer coating for ultrafast separation of water-in-oil emulsions

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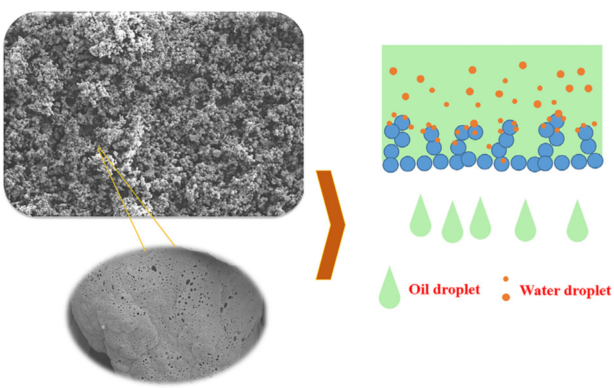
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 August 2017
Revised 16 September 2017
Accepted 19 September 2017
Available online 23 September 2017

Keywords:
One-step preparation
ABS coating
Superhydrophobic
Water-in-oil emulsions
Efficient

ABSTRACT

Hypothesis: Superhydrophobic membranes with opposite wettability toward water and oil are able to separate water-in-oil emulsions. By constructing porous and hierarchal-structured superhydrophobic coating on filter paper, we hope a quick separation process could be achieved due to the acceleration of both demulsification and penetration process.
Experiments: Here, superhydrophobic coatings were prepared by simply spraying environmental and cost-effective acrylonitrile-butadiene-styrene copolymer (ABS) colloid in dichloromethane onto filter paper. The morphologies and wettability of the obtained coatings were carefully studied. Moreover, the separation performances in dealing with various surfactant-stabilized water-in-oil emulsions (SSWOE) were also investigated to verify our hypothesis.
Findings: The morphologies of the ABS coatings varied with its weight concentration in dichloromethane and they changed from porous and plain surface into porous and hierarchal-structured surface. Besides, the hydrophobicity of the above coatings varied form hydrophobic to superhydrophobic. Moreover, the resulted superhydrophobic membranes show great separation capability in separating various span 80-stabilized water-in-oil emulsions with oil filtrate purities larger than 99.90% and huge penetration fluxes whose maximum is over 13,000 L/(m^2 h). Thus, we envision that such membrane can be a practical candidate in dealing with water-in-oil emulsions to obtain pure oils.

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https://doi.org/10.1016/j.jcis.2017.09.070
0021-9797/

1. Introduction

Oils, the principal resource in industry, play an increasingly critical role in current world with the development of economics. The purity of oil is crucial for their excellent performance [1,2]. The insistent demand for very pure oils in various industries drives researchers to distill them from water-in-oil emulsions as efficiently as possible. However, traditional oil-water separation approaches such as oil skimmers and centrifuge technology function well only in separating immiscible oil/water mixtures but fail to deal with emulsified oil/water mixtures especially those stabilized by surfactants [3–5]. Water-in-oil emulsions always have very small dispersed water droplets in oil phase and are very stable, which make it difficult to perform successful separation [6]. Based on the sieve effect, micro-filtration [7] and ultrafiltration [8] membranes with small pores are prevailing in purifying water-in-oil emulsions. Nevertheless, shortcomings of them still exist and will hinder their wide application. Both oils and surfactants dissolved into oils to stabilize the emulsions can block the penetration pores on the membranes during the separation process. On account of these, penetration fluxes and efficiencies of these membranes will decrease very fast as separating processes proceed. Moreover, these approaches always necessitate huge energy and take a long time because of low fluxes, impeding their utilization in tackling large volumes of emulsions. To overcome their shortcomings, materials with special wettability toward water and oils have been extensively reported to separate oil/water mixtures recently [9–12]. These membranes can separate oil/water mixtures by selectively resisting one phase and allowing the other phase to penetrate at the same time. To date, only few of them has achieved the separation of SSWOE with water droplet size smaller than 20 μm [13,14].

In order to prepare superhydrophobic materials, both hierarchal-structured surfaces and modification are necessary [15]. Various methods have been used to fabricate rough surfaces such as hydrothermal method [16], microwave technology [17] and so on [18–20]. As for the superhydrophobic membranes to separate SSWOE, two main approaches are convenient to realize this goal: fabricating porous and ultra-hydrophobic membranes straightforwardly; coating pristine porous membranes with hydrophobic materials. Both of them can form porous and hierarchal-structured surfaces and be promising in separating SSWOE. Over the past years, various superhydrophobic and porous membranes have been utilized to demulsify SSWOE and separate them [21–25]. Inspired by *Stenocara* beetles, Zeng et al. incorporated superhydrophobic nano-coatings and superhydrophilic micro-bumps on stainless mesh to successfully separate SSWOE with oil purity higher than 99.9% [26]. Zhang et al. fabricated super hydrophobic/superoleophilic PVDF membrane to purify microemulsions using phase inversion process [27]. All these materials succeeded in demulsifying emulsions and separating them effectively. Nevertheless, sophisticated processes and costly raw materials are still necessary to prepare these membranes, hindering their mass production. Furthermore, the gravity-driven oil permeation fluxes in these reports are inadequate in tackling large volumes of SSWOE. For the former one, a one-step preparation process using common instruments and cost-effective stuffs to achieve superhydrophobic membranes can satisfy the need of mass production. For the latter one, according to the Hagen-Poiseuille equation:

$$J = \varepsilon\pi r^2 \Delta P / 8\mu L$$

(where J is the penetration flux, ε is the porosity, r is the effective pore radius, ΔP is the pressure, μ is the liquid viscosity and L is the thickness of the membrane) [28], it is significant to enhance the porosity and decrease the pore size of the membranes to achieve huge fluxes in the case of other factors unchanged. Such materials are prospective in efficient and ultrafast separation of SSWOE yet still something of a rarity.

Superhydrophobic coatings based on colloid and interface science have caught increasing attention due to its cost-effective raw materials and the capacity of converting different substrates into superhydrophobic surfaces. Based on Wenzel equation ($\cos\theta^* = r\cos\theta$, where θ^* is the contact angle of rough surfaces, r is the roughness factor and θ is the contact angle on flat surfaces) [29], both hydrophobicity and hydrophilicity is in proportion to surface roughness. Considering that the coatings are usually coarser than the pristine surfaces, it will be tenable to prepare superhydrophobic surfaces through constructing micro-scale or nano-scale rough hydrophobic coatings onto versatile substrates including porous membranes. In recent years, phase inversion [5,27], electro-spinning [12] and sol-gel technology [24] based on colloid property have been widely applied in hydrophobic materials for oil/water separation. They are effective but still not that convenient for mass production owing to their complicated preparation processes. Wang et al. sprayed suspensions of edible materials onto substrates and the superhydrophobic coatings with hierarchal and coarse morphologies were obtained [30]. However, they were not porous and thus couldn't allow oils to permeate, making them impossible to be applied to separate oil/water mixtures.

In this paper, inspired by the previous works, we report a novel superhydrophobic ABS coating for highly efficient and ultrafast separation of SSWOE. With abundant methylene and phenyl groups, ABS resin is slightly hydrophobic (see Fig. S1). After the ABS colloids were sprayed onto filter paper (average pore size: 15–25 μm, see Fig. S2), it was amazing that the obtained coatings have unique porous and hierarchal structure. Such unique structure enhances the hydrophobicity of ABS, which, as a result, imparts it remarkable ability of separating SSWOE with fluxes about 13140 L/(m^2 h) and oil purity higher than 99.9% driven solely by gravity. Considering the simple and cost-effective preparation process, we believe that it is promising to address the problem of mass SSWOE and purify versatile oils.

2. Experimental section

2.1. Materials

All the oils (analytical reagent) including isooctane, petroleum ether, cyclohexane and the solvent dichloromethane were obtained from Shanghai RichJoint Chemical Reagents Co., Ltd. Span 80 (chemically pure) was bought from Shanghai Mackliln Biochemical Co. Ltd. ABS was supplied by Dongguan Suheng Plastics Co., Ltd. Filter paper with average pore size 17–25 μm was bought from a local store.

2.2. Preparation process

At first, 0.15, 0.3, 0.45 and 0.6 g of ABS resins were dissolved into 25 mL of dichloromethane respectively to form different ABS colloids. Then, the ABS colloids with different weight concentration (6, 12, 18, 24 g/L) were sprayed onto different substrates using an airbrush from a distance about 18 cm to form ABS-***n*** (***n*** = 6, 12, 18, 24). The spraying pressure was about 0.3 Mpa.

2.3. Separation process

Different span 80-stabilized water-in-oil emulsions were prepared firstly. 0.05% weight concentration of span 80 was dissolved into 50 mL of different oils with stirring. Then, 0.5 mL of deionized