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Design of a superhydrophobic and superoleophilic film using cured fluoropolymer@silica hybrid

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ABSTRACT

Recently, considerable efforts have been made on superhydrophobic–superoleophilic filter to satisfy the requirements of the applications to oil/water separation. In this work, we obtained a superhydrophobic and superoleophilic film by coating cured fluoropolymer@silica hybrid on stainless steel mesh. Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric-differential scanning calorimetry (TG-DSC) were used to determine the chemical composition and thermal stability of the sample. The effect of silica nanoparticles (NPs) concentration on the surface property of the hybrid film was analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle analyzer. The results indicate that silica NPs not only enhance the thermal stability, but also strengthen the hydrophobicity and oleophilicity of the film. When 20 wt% silica NPs was added into the thermosetting fluoropolymer, the hybrid film shows both superhydrophobicity and superoleophilicity owing to the large surface roughness factor (RMS) and porous structure. Moreover, the hybrid film could be used to separate water from different oils effectively. When the pore size of the mesh is less than 300 μm, the oil/water separation efficiency of the film reaches above 99%, which shows a great potential application to dehydrate fuel oils.

1. Introduction

With the development of aviation and automobile industry, the requirement of engine in planes or cars is higher and higher. Oil, as "blood" in engine, plays a crucial and important role in operational life span and service efficiency of engine. However, oil in engine usually contains some water, which can accelerate the deterioration of oil and destroy the engine. Therefore, the effective removal of water from oil is a big issue for modern industry. Among oil/water separation technologies, coalescence separation technology has been widely used in virtue of its large processing capacity and low energy consumption and economic cost [1]. As the illustration of the operation principle of a coalescence separator in Scheme 1, the mixture of oil and water first passes through a coalescer filter to form large water droplets to break the emulsion. Then the separation of water and oil was achieved under gravity by a separating filter. Usually, the separation filter is made by hydrophobic and oleophilic materials coated on metal meshes, and the oil/water separation efficiency is highly related to its wettability [2]. Recently, many works have been devoted to the preparation of superhydrophobic-superoleophilic films for their exciting applications in oil/water separation [3,4]. Among the reported films, inorganic nanomaterials such as SiO_2 [5–7], TiO_2 [8,9], ZnO nanorod [10–12], carbon nanotube [13,14], copper hydroxide nanowire [15,16], etc. are commonly used, because they could construct micro-nano binary structures for the sake of superhydrophobicity or superoleophilicity. However, some prepared superhydrophobic films are not stable, especially in high hydraulic pressure of the flow of oil/water mixture. In addition, some nanoparticles are prone to be detached from the substrate, which may cause wear and tear on the engine. Therefore, developing a stable superhydrophobic and superoleophilic film that makes nanoparticles firmly attach on the substrate is emergent and necessary for practical application [7,17,18]. In our previous work, we fabricated silica film with superhydrophobicity and superoleophilicity on stainless steel mesh, which proved the oil/water separation capacity [19,20]. However, the adhesion force between silica nanoparticles (NPs) and mesh was weak because of the lack of chemical band between them. Further, we incorporated fluorinated polymers with silica NPs to fabricate composite films to solve this problem, and found that the

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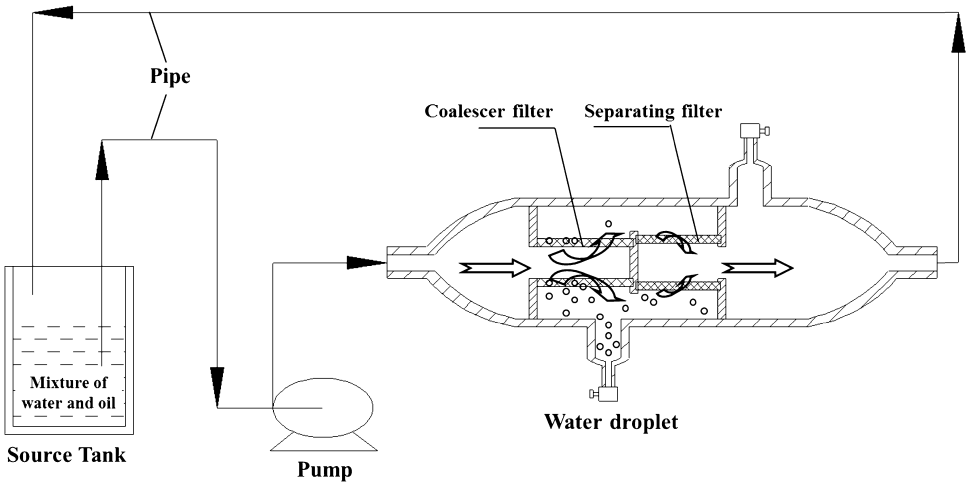

Scheme 1. Schematic diagram of a coalescence separator for oil/water separation.

chemical composite of the fluorinated polymers could switch the wettability of the film [21]. In this paper, we investigated the effect of silica NPs on the wettability of the composite films in detail, and determined the oil/water separation efficiency of the films under different conditions.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), stearyl methacrylate (SMA) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Guangzhou Shuangjian Trading Co., Ltd., China. Perfluoroalkyl ethyl methacrylates ($C_nF_{2n+1}CH_2CH_2OOC(CH_3)C{=}CH_2$ (n = 6,8,10), FMA) was from Shanghai Fchemicals Technology Co., Ltd., China. Silica aerogel (R974, hydrophobically modified by dimethyldichlorosilane DDS) was from Degussa Evonik. HDI trimer was purchased from Bayer. 2,2-azobisisobutyronitrile (AIBN) was from Tianjin Kemiou Chemical Reagent Co., Ltd and recrystallized before use. Stainless steel mesh, petrol, kerosene, diesel and hydraulic oil were purchased from local market.

2.2. Preparation of fluoropolymer@silica hybrid film

In a typical experiment, 5 g FMA was added into 50 g solution of butyl acetate and xylene (V/V=1:1) with vigorous stirring and refluxed at 80 °C for 30 min. Then 20 g MMA, 15 g SMA, 10 g HEMA and 0.75 g AIBN were mixed, followed by adding the mixture slowly into the reaction system dropwise within 2 h. After 4 h refluxing of the reaction mixture at 80 °C, fluoropolymer was obtained.

The fluoropolymer@silica hybrid films were prepared by mixing 10 g fluoropolymer and different weights of silica aerogel in 190 g solution of butyl acetate and xylene (V/V = 1:1), then 1 g HDI trimer was added with continuous stirring, finally the stainless steel mesh were put into the mixtures and cured at 110 °C for 2 h.

2.3. Characterization

The chemical compositions of silica, fluoropolymer and fluoropolymer@silica hybrid were characterized by Fourier transform infrared spectroscopy (FTIR, Vector 33, Bruker, Germany). X-ray photoelectron spectroscopy (XPS) data were collected in both survey and high-resolution mode on Kratos Axis Ultra DLD systems equipped with Al K α X-ray source and operating at 300 W. The surface morphology of hybrid film was observed by scanning electron microscopy (SEM, LEO 1530VP, Germany). The surface roughness of the hybrid was characterized by atomic force microscope (AFM, CSPM5000, Benyuan, China). The thermal stability of fluoropolymer and fluoropolymer@silica hybrid were computed by thermogravimetric-differential scanning calorimetry (TG-DSC, Netzsch STA449C, Germany) by heating the sample (8 mg) in a flow of air (30 mL/min) at 10 °C/min from room temperature to 600 °C. Static contact angle (CA) measurements were performed with an optical contact angle meter (OCA20 Micro, Dataphysics, Germany). The wettability of the hybrid films was determined by measuring CAs of two probe liquids: water and kerosene.

3. Results and discussion

Fig. 1 shows FTIR spectra of silica, fluoropolymer and fluoropolymer@silica hybrid. In the IR spectrum of silica, two characteristic peaks at 3436 and 1631 cm^{-1} were ascribed to physically absorbed water. Three peaks at 1108, 811 and 474 cm^{-1} were attribute to absorption peak of Si-O-Si band. No peak at 960 cm^{-1} was observed, indicating the absence of Si-OH group. Besides, the weak peak emerging at 2967 cm^{-1} could be ascribed to stretching vibration of C-H band, indicating that the hydrophobic silica NPs were modified by alkyl groups. In the IR spectrum of fluoropolymer, three peaks at 2992, 2926 and 2854 cm^{-1} were associated with methyl or methylene groups. The strong peak at 1731 cm^{-1} was ascribed to the stretching vibration of carbonyl group, indicating the presence of methacrylate. Two peaks at 1452 and 1388 cm^{-1} were characteristic peaks of MMA, and another two peaks at 1243 and 1151 cm^{-1} were attributed to —CF_2 and —CF groups from FMA. The peak at 750 cm^{-1} could be ascribed to —$(CH_2)_n$— ($n \geq 4$) groups from SMA. At 3524 cm^{-1}, the absorption band belonged to stretching vibration of -OH group from HEMA. Meanwhile, the double bond at 1640 cm^{-1} did not appear, which implied that MMA, SMA, FMA and HEMA monomers have been copolymerized. The above data demonstrated that the fluoropolymer consisted of MMA/SMA/HEMA/FMA. Compared with silica and fluoropolymer spectra, some new peaks emerged in fluoropolymer@silica spectrum. For example, the peak at 3397 cm^{-1} was ascribed to —NH group, and the peak at 1735 cm^{-1} was ascribed to —NH—COO— group. Another two peaks at 1692 and 1529 cm^{-1} belonged to —NH—CO—NH— group and —C—N— group, respectively, which demonstrated the characteristic groups of polyurethane. The weak peak at 2277 cm^{-1} was ascribed to the remaining —NCO— group from HDI trimer. Besides, the peak at 3524 cm^{-1} in fluoropolymer disappear in fluoropolymer@silica hybrid, which proves

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