



Robust superhydrophobic and superoleophilic filter paper via atom transfer radical polymerization for oil/water separation

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ABSTRACT

Robust superhydrophobic and superoleophilic cellulose-g-PFOEMA filter paper membranes were fabricated via surface grafting of poly(perfluorooctylethyl methacrylate) (PFOEMA) using atom transfer radical polymerization (ATRP). The surface chemical compositions, morphologies and wettability of cellulose-g-PFOEMA with different degree of graft ratio (DG) were investigated using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and contact angle (CA) measurement. IR and XPS showed that PFOEMA were introduced into surface of filter paper. The superhydrophobicity of filter paper increased with amount of PFOEMA grafted. When DG of grafted PFOEMA was higher than 11.2%, the superhydrophobicity reached a steady state and the measured water contact angle was about 157°. The PFOEMA-grafted filter paper exhibited excellent chemical resistance toward a wide range of pH solution from 1 to 12. Cellulose-g-PFOEMA is convenient for oil/water separation with efficiency higher than 95%. The excellent reusability and stability make cellulose-g-PFOEMA filter paper membrane a promising candidate in the applications of oil spillage cleanup and the separation of oil/water mixture.

1. Introduction

Materials with extreme wettability, including superhydrophobic, superoleophilic, superhydrophilic, and superoleophobic, have attracted considerable academic and industrial interest in the past decades due to their promising potential applications in self-cleaning, anti-icing, anti-fouling, smart membrane, microfluidic devices, and oil/water separation (Chen et al., 1999; Wang, Liu, Yao, & Jiang, 2015). Some creatures in nature, such as lotus leaves, cicada wings, and mosquito eyes, present fascinating superhydrophobicity. A droplet of water on its surface remains almost spherical and easily rolls off, removing dirty substances in their path. Fish scales of *Crucian Carp* exhibit superoleophilicity in air and superoleophobicity underwater. A thin layer of mucus and multi-scale structures could trap water and form a composite interface to resist oil. Especially, functional materials integrated with both superhydrophobicity and superoleophilicity, were effective in the oil/water separation, which might play an important role in oil spill accidents and the increasing industrial oily wastewater. Bioinspired combination of low surface-energy substances and hierarchical micro/nanostructured surface, a variety of artificial superhydrophobic/superoleophilic materials have been developed, e.g., carbon nanotube sponge (Gui et al., 2010), metal mesh (Wang, Song, & Jiang, 2007), and polymers (Zhang

et al., 2016; Zhang & Seeger, 2011).

With the increasing environmental interest in the use of renewable resources and biodegradable materials, cellulose has attracted intense attention for the fabrication of functional superhydrophobic and superoleophilic materials. Cellulose is one of the most common organic polymers in nature and is considered as an almost inexhaustible source of raw material for the increasing demand in environmentally friendly and biocompatible products in coating, laminates, optical film, sorption media, pharmaceuticals, foodstuffs, and cosmetics (Joubert, Musa, Hodgson, & Cameron, 2014; Tian & He, 2016). However, due to the large number of hydroxyl groups on surface of filter paper, cellulose is hydrophilic and easily wetted by water. To meet the practical application, physical or chemical modifications like coating (Du, Wang, Chen, & Chen, 2014; Gao et al., 2015; Li, Yang, Li, Lan, & Peng, 2017; Li, Zhang, & Wang, 2008; Lin et al., 2016; Wang, Li, & Lu, 2010; Wen, Guo, Yang, & Guo, 2017; Zhang, Lu, Qian, & Xiao, 2014; Zhao, Xu, Wang, & Lin, 2012), acetylation (Frisoni et al., 2001; Zhou et al., 2016), silylation (Andresen, Johansson, Tanem, & Stenius, 2006; Goussé, Chanzy, Excoffier, Soubeyrand, & Fleury, 2002; Sai et al., 2015), and graft polymerization (Carlmark & Malmstrom, 2002; Deng et al., 2010; Gao et al., 2016; Guo, Wang, Shen, Shu, & Sun, 2013; Jain, Xiao, & Ni, 2007; Larsson, Pendergraph, Kaldeus, Malmstrom, & Carlmark, 2015; Li

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et al., 2015; Lindqvist et al., 2008; Meng et al., 2009; Nystrom, Lindqvist, Ostmark, Hult, & Malmstrom, 2006; Xiao, Li, Chanklin, Zheng, & Xiao, 2011; Xue, Guo, Ma, & Jia, 2015; Zampano, Bertoldo, & Bronco, 2009), are generally applied to adjust the surface property.

Among those various preparation methods, the graft polymerization technique is an versatile method to bond hydrophobic polymers covalently onto cellulose and has been the subject of intensive research (Carlmark & Malmstrom, 2002; Deng et al., 2010; Gao et al., 2016; Lindqvist et al., 2008; Meng et al., 2009; Nystrom et al., 2006; Xiao et al., 2011; Zampano et al., 2009). The covalent bonds formed between cellulose and polymers enhance the stability of the superhydrophobicity and prolong the lifespan of the superhydrophobic material. Under radiation-induced graft polymerization, 1H,1H,2H,2H-nonafluorohexyl-1-acrylates were grafted onto the cotton fabric (Deng et al., 2010). The modified cotton fabric exhibited superhydrophobicity and the reported water contact angle was approximately 160°. However, the water droplets pinned on the surface and were unable to slip off irrespective of the direction in which the surface is tilted.

Surface-initiated atom transfer radical polymerization (SI-ATRP) is a versatile approach for the polymers to grow from initiating sites or immobilized initiators on the surface of cellulose, providing graft chains with controllable molecular weight and narrow molecular weight distribution (Joubert et al., 2014; Matyjaszewski & Xia, 2001). Carlmark et al. reported that poly(methyl acrylate) was grafted from filter paper by SI-ATRP. The grafted paper became more hydrophobic with an increase in grafted chain lengths and the contact angle reached 133° (Carlmark & Malmstrom, 2002). Wood pulp cellulose fibers were grafted with poly(ethyl acrylate), which is of great potential as value-added paper products (Zampano et al., 2009). Xiao et al. demonstrated poly(butyl acrylate)-grafted cellulose microfibrils (CMF) with controllable hydrophobic chains by varying the reaction temperature, the type of solvents, and the use of catalyst (Xiao et al., 2011). This hydrophobic-modified CMF is a promising reinforcement for biocomposites.

Cellulose-based filter paper is a porous microtextured material with the capability for rapid liquid–liquid and solid-liquid separations. Although many hydrophobic monomers (Carlmark & Malmstrom, 2002; Deng et al., 2010; Joubert et al., 2014; Lindqvist et al., 2008; Meng et al., 2009; Nystrom et al., 2006; Xiao et al., 2011; Zampano et al., 2009) have been used to graft onto cellulose, the fabrication of functional cellulose-based membranes with both superhydrophobicity and superoleophilicity has not been explored extensively. It is desirable to fabricate filter papers with superwettability by graft polymerization for the oil/water separation in the complicated practical applications.

In this study, a robust superhydrophobic and superoleophilic filter paper membrane was prepared by grafting of poly(perfluorooctylethyl methacrylate) (PFOEMA) on filter paper using ATRP method. The covalent chemical bond linking between low-surface-energy PFOEMA and filter paper surface provides high chemical resistance to withstand various harsh conditions such as acidic or alkaline solutions. The PFOEMA-modified filter paper has high efficiency and reusability for the separation of oil/water mixture by a simple and convenient filter approach.

2. Materials and methods

2.1. Materials

Filter papers were purchased from Hangzhou Special Paper Co., Ltd, China. 2-(perfluorooctyl)ethyl methacrylate (FOEMA, 97%) were obtained from Shanghai Aladdin Reagent Co., Ltd, China. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%) and 2-bromisobutyl bromide (BiBB, 98%) were obtained from Tokyo Chemical Industry. Copper (I) bromide (CuBr, > 99%) were purchased from Adamas. *N,N*-dimethylformamide (DMF), dichloromethane (CH₂Cl₂), toluene,

pyridine, acetone, and ethanol were supplied by Shanghai Aladdin Reagent Co., Ltd, China. All reagents were analytical grade and used as received. Ultrapure water (18.2 MΩ cm) obtained from a water purifier (Sichuan Water Purifier Co. Ltd., China) was used for all experiments.

2.2. Immobilization of BiBB on filter paper

BiBB was used as the initiator for attachment to the cellulose surface. Prior to immobilization of the initiator, the pristine filter paper with diameter of 9 cm was ultrasonicated for 5 min in ethanol and acetone. The filter paper was immersed into a solution containing BiBB (0.4 mL, 3.23 mmol), pyridine (0.26 mL, 3.23 mmol) and CH₂Cl₂ (15 mL). After the solution was stirred for 4 h at room temperature, the cellulose-based macroinitiator with Br-end was formed, which is coded as Cellulose-Br. Cellulose-Br was thoroughly washed with ethanol and water to remove residual reactants, and dried under vacuum at 50 °C overnight.

Based on the proportion of the C and Br obtained from elemental analysis, the degree of substitution (DS) of the surface of Cellulose-Br was evaluated by the following equation (See Supplementary Information):

$$DS = \frac{6A_C}{A_C - 4A_{Br}} \quad (1)$$

where A_C and A_{Br} represent the atomic percentage of C and Br, respectively.

2.3. Grafting of FOEMA from cellulose-Br

Cellulose-Br was immersed in a round-bottom flask containing DMF (200 mL), CuBr (25.0 mg, 0.14 mmol), and PMDETA (29 μL). A determined amount of FOEMA monomer (307, 265, 212, 201, 186, 175, 159, 143, 117, 106, 95, 90, 74, 69, and 53 μL) was subsequently added to obtain samples with different degree of graft ratio (DG). After removing oxygen by freeze-pump-thaw cycles for 5 times, the polymerization tube was charged with nitrogen. The reaction mixture was stirred at 60 °C for 4 h. After the reaction, the FOEMA-modified filter paper, which is coded as cellulose-g-FOEMA, was successively washed with 0.3 M oxalic acid, ethanol, and H₂O to remove the residual monomer and catalyst thoroughly, and dried under vacuum at 50 °C overnight.

The DG of cellulose-g-FOEMA was determined as the weight of the sample increases, according to the following equation (Deng et al., 2010):

$$DG = \frac{W_g - W_0}{W_0} \times 100\% \quad (2)$$

where W_g and W_0 are the weights of the sample after and before grafting, respectively.

2.4. Characterization

The surface morphologies were observed using a Hitachi S4800 field emission scanning electron microscope (FESEM). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were recorded on a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrometer equipped with a MKII Golden Gate, single reflection ATR System from Specac Ltd., London, U.K. The surface was pressed against the ATR crystal to obtain a sufficient signal. Contact angle (CA) measurements were performed using a dynamic drop tension meter (DSA 30, KRÜSS, Germany). The water contact angles of the filter paper with different DG were measured by placing a 5 μL water drop on the surface of filter paper, which were average values of five different points on each sample surface. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a PHI LS 5600 instrument with a standard Mg Kα X-ray source. The energy resolution of the

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