Fabrication of Oil-Water Separation Filter Paper by Simple Impregnation with Fluorinated Poly-Acrylate Emulsion

Tian Yu, Guilong Xu*, Xiwen Wang, Jin Yang, and Jian Hu

A fluorinated poly-acrylate emulsion with various fluorine contents was prepared by a seeded semi-continuous emulsion polymerization method and applied to filter paper for oil-water separation applications. The effects of surface wetting behavior on the oil-water separation efficiency of the prepared filter paper were studied. The results show that the prepared highly hydrophobic and superoleophilic filter paper presented 94.45 wt% water separation efficiency and strong mechanical strength. In addition, the oil-water separation stability and durability of the filter paper were also tested and shown to be suitable for use in real oil-water separation applications. These properties indicate that the filter paper has great potential applications in the oil-water separation industry.

Keywords: Fluorinated poly-acrylate emulsion; Filter paper; Oil-water separation

*Contact information: State Key Lab of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China; *Corresponding author: feglxu@scut.edu.cn*

INTRODUCTION

Owing to the increasing environmental pollution accompanying the development of industry and society, there is a growing demand for functional materials in the fields of oil-water separation, oil spill cleanup, *etc*. (Adebajo *et al.* 2003; Hubbe *et al*. 2013). The conventional methods used to solve these problems include combustion, oil skimmer vessels, and absorbent materials (Choi and Cloud 1992). However, the combustion method may cause severe air pollution, oil skimmer vessels have low efficiency, and traditional absorbent materials can have poor selectivity and recyclability. Recently, surfaces with both superhydrophobic and superoleophilic properties have attracted considerable interest in the oil-water separation field because they can only be wetted by oil while repelling water completely; they therefore exhibit high oil-water separation efficiency. Several materials for oil-water separation application have been fabricated based on this principle, *e.g.*, composite polymer films (Zhang *et al*. 2006), mesh films (Pan *et al*. 2008; Cheng *et al*. 2011), cotton textiles (Xue *et al*. 2008), membranes (Zhang *et al*. 2013), and carbon nanotube sponges (Lee and Baik 2010). These materials have been used for separating small amounts of water from oil. Nevertheless, they have limitations for practical applications due to high cost, complex preparation processes, or difficulty in scalable fabrication. Filter paper, a porous filter material, has characteristics of high absorption ability, low cost, and easily scalable fabrication. However, in addition to its low mechanical strength, filter paper absorbs both water and oils (or organic solvents); these attributes make it impractical for oil-water separation. Therefore, it is essential to alter the filter paper properties to make the material both hydrophobic and oleophilic, while at the same time providing sufficient mechanical strength for practical oil-water separation applications in the automobile industry.

To the best of our knowledge, few works have reported filter paper with superhydrophobic/highly hydrophobic and superoleophilic properties for oil-water separation applications. Quan *et al*. (2009) and Werner *et al*. (2010) prepared superhydrophobic paper with the inexpensive and common chemical Alkyl Ketene Dimer (AKD) or a crystallizing wax by supercritical carbon dioxide, but we can infer that paper coated by AKD or wax cannot be used effectively in oil media or be mechanically strong enough for an automobile engine system. Wang *et al*. (2010) and Zhang *et al*. (2012) successfully prepared a superhydrophobic and superoleophilic filter paper by treating commercially available filter paper with a mixture of hydrophobic silica nanoparticles and polystyrene solution in toluene; however, their methods are tedious and use large amounts of toluene, which is not environmental friendly. In our contribution, a fluorinated poly-acrylate (FPA) emulsion was prepared and coated on the filter paper surface by a simple drop-coating procedure. The FPA emulsion can change the surface wetting behavior of the filter paper from hydrophilic and oleophilic to hydrophobic and oleophilic and can also strongly enhance its mechanical strength. The effects of the wetting behavior of the FPA coating filter paper on the water-oil separation efficiency were studied.

EXPERIMENTAL

Materials

Dodecafluoroheptyl methacrylate (DFMA, 96+ %) was obtained from XEOGIA Fluorine-Silicon Chemical Co. Ltd., China. Triethylene glycol dimethacrylate (TrEGDMA, 96+ %), ammonium allyloxtmethylate nonylphenol ethoxylates sulfate (DNS-86, 96+ %), and stearyl methylacrylate (SMA 96+ %) were purchased from Guangzhou Shuangjian Co. Ltd., China. Butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA), ammonium persulfate (APS), and sodium bicarbonate ($NaHCO_3$) were purchased from Guangdong Guanghua Chemical Factory Co. Ltd., China in their reagent grade and used as received.

Filter paper was provided by Guangzhou Vanken Special Material Science and Technology Development Co. Ltd., China.

Water was purified by a Milli-Q system (Millipore, Massachusetts, USA).

Synthesis of FPA Emulsion

An FPA emulsion was prepared by a seeded semi-continuous emulsion polymerization technique. All the polymerizations were carried out in a 500-mL four-neck flask equipped with a reflux condenser, mechanical stirrer, and dropping funnels and heated in a water bath.

The pre-emulsified first-stage monomers were obtained by emulsifying the core monomers in a mixture of 30 g of water and 0.50 g of DNS-86 at room temperature for about 30 min. Then, 20.0 wt% of the pre-emulsified core monomers and 40.0% of the initiator solution (0.64 g of APS dissolved in 30 g of water) were added to a flask containing 70 g of water, 0.90 g of DNS-86, 30 g of ethanol, and 0.50 g of buffering agent ($NaHCO_3$) and the temperature was raised to 77 °C. After an additional 30 min of equilibration time, the remaining mixed monomers and initiator were added to the flask drop-by-drop simultaneously within 2 h. The pre-emulsified second-stage monomer mixture was then fed into the flask containing the above poly-acrylate (PA) seed latex by the starved-feed addition method. The second-stage APS aqueous solution was also fed into the flask at the same pace as the pre-emulsified shell monomers. After feeding, the temperature was maintained at 80 °C for another 2 h. The obtained latex was cooled to room temperature, and $NH_3 \cdot H_2O$ was used to adjust the pH value of the final latex to approximately 7.0 to 8.0. Recipes for the preparation of the FPA emulsion are given in Table 1.

Table 1. Recipes for the Preparation of FPA Emulsion

Sample	F_0	F_1	F_2	F_3	F_4	F_5	F_6
First stage							
MMA	40.00	40.00	40.00	40.00	40.00	40.00	40.00
BA	26.00	26.00	26.00	26.00	26.00	26.00	26.00
MAA	2.00	2.00	2.00	2.00	2.00	2.00	2.00
TrEGDMA	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Second stage							
MMA	16.00	14.50	13.00	11.50	10.00	8.50	7.00
SMA	3.00	3.00	3.00	3.00	3.00	3.00	3.00
BA	11.00	9.50	8.00	6.50	5.00	3.50	2.00
DFMA	0	3.00	6.00	9.00	12.00	15.00	18.00
TrEGDMA	0.50	0.50	0.50	0.50	0.50	0.50	0.50
All reported amounts are in grams							

Preparation of Oil-Water Separation Filter Paper

The prepared FPA emulsion was diluted to a concentration of 4.0 wt%; then, pristine filter paper was dipped into the diluted emulsion. After the pristine filter was completely wetted, the wetted paper was removed and dried in an oven at 130 °C for 30 min. The impregnated resin accounted for 20 ± 1 wt% of the pristine paper.

Characterization

Infrared (IR) spectra were acquired on a Fourier transform infrared spectrometer (Burke Company, Germany).

The contact angles (CAs) of liquid on the FPA films and coated filter paper were measured using an OCA15 (Data Physics Instruments Company, Germany). The reported contact angle is the average of five individual test values at different locations on the polymer or filter paper surfaces.

Scanning electron microscopy (SEM) observation was performed using a scanning electron microscope (S-3700N, Japan).

A stiffness tester (TMI 79-25-00-0002, USA), bursting strength tester (L&W CE-180, Sweden), and tensile strength tester (L&W SE-062, Sweden) were used to measure the stiffness, bursting strength, and tensile strength (average of 10 test values), respectively, of the experimental filter paper.

RESULTS AND DISCUSSION

IR Analysis

Figure 1 shows the IR spectra of FPA (curve a) and PA (curve b) emulsion polymer films.

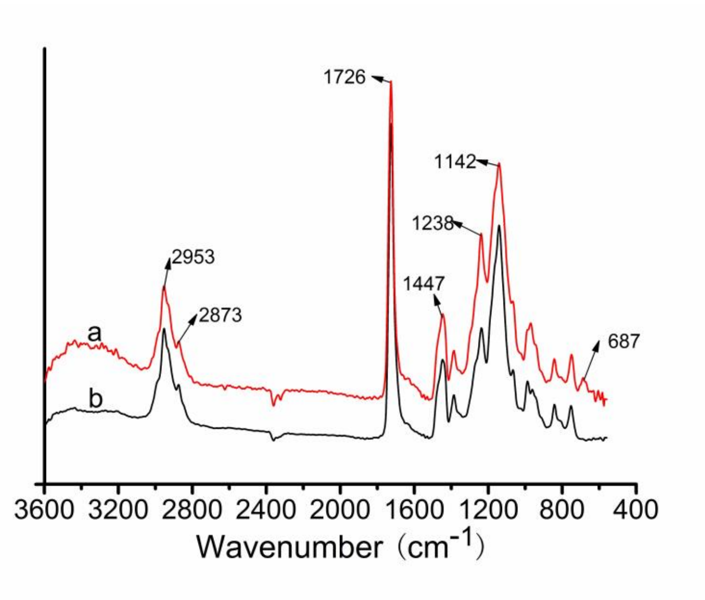

Fig. 1. IR spectra of the FPA (curve a) and PA (curve b)

As shown in Fig. 1, the outline of the FPA spectrum (curve a) was similar to that of the PA spectrum (curve b). Both of the spectra exhibited the characteristic stretching and distortion vibration peaks of C-H (CH_2) at 2953, 2873, and 1447 cm^{-1}, stretching vibration of C=O at 1726 cm^{-1}, and asymmetrical and symmetrical stretching vibrations of C-O at 1238 and 1142 cm^{-1}, respectively. Comparing the IR spectrum of FPA with that of PA, the weak absorption band at 687 cm^{-1} can be assigned to the wagging vibration of -CF_2 groups (Cheng *et al.* 2007; Xiong *et al.* 2010; Yang *et al.* 2007). Furthermore, the stretching vibration of -CF_2 and -CF_3 groups at about 1289 to 1100 cm^{-1} and asymmetrical stretching vibration of C-O at 1238 cm^{-1} overlapped with each other (Cheng *et al.* 2007; Xiong *et al.* 2010; Yang *et al.* 2007). This resulted in broadening of the absorption peaks at 1100 to 1240 cm^{-1} compared with that of the non-fluorinated PA emulsion. Moreover, there was no adsorption peak at 1640 cm^{-1}, commonly attributed to characteristic C=C monomer bonds. All of the IR analysis results indicated that all the monomers could be introduced into the latex particles as desired through emulsion polymerization.

Application of Filter Paper in Water–Oil Separation

As shown in Fig. 2, when a water droplet was placed on the coated paper surface, a nearly spherical water droplet was formed and steadily stayed on the paper for extended periods of time. However, a diesel oil droplet completely wetted the coated filter paper immediately, which indicates that the filter paper possessed properties of high hydrophobicity and superoleophilicity simultaneously.

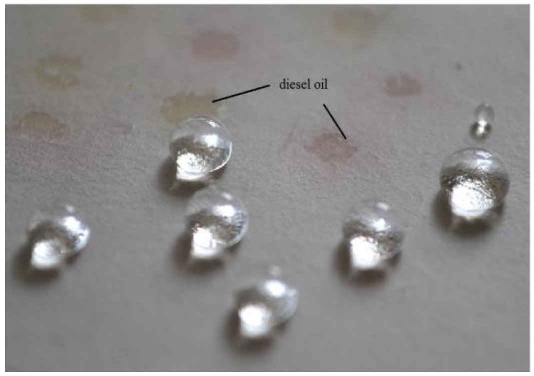

Fig. 2. Coated filter paper with oil and water droplets

Figure 3 shows the equipment used for the oil-water separation process. The oil-water mixture consists of 90 mL of diesel oil and 10 mL of water. After vigorous stirring for approximately 30 min, the mixture was poured onto the FPA coated filter paper. Oil was able to freely pass through the coated filter paper at atmospheric pressure and accumulate into the measuring cylinder beneath. During this process, water was blocked and collected on the filter paper. The water separation efficiency of the filter material was defined as the weight ratio of the collected water to the added water.

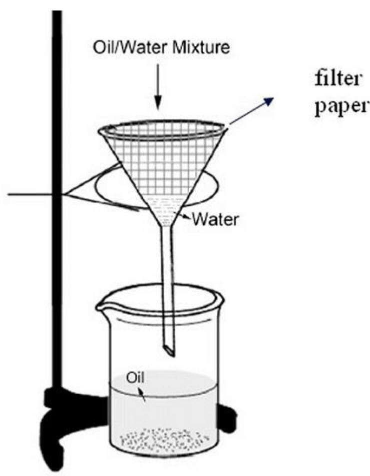

Fig. 3. Oil-water separation efficiency measurement equipment

The water separation efficiency is reported as the average of five individual test values, and the results are shown in Table 2.

Table 2. Contact Angles and Water Separation Efficiency of Filter Papers

Sample	WCA (º)	OCA (º)	WCA on coated filter paper (º)	Oil drop completely wet the filter paper(s)	Separation efficiency (wt%)
F0	77.9	21.3	103.8	immediately	79.42
F1	93.4	31.3	116.6	immediately	85.96
F2	98.6	36.6	122.8	about1s	89.25
F3	102.3	39.8	128.8	1-2 s	91.03
F4	104.9	41.2	130.3	2-3 s	94.45
F5	105.4	46.7	131.2	9-10 s	90.64
F6	106.2	62.3	132.5	~30 s	87.21

From Table 2, it is clear that oil and water contact angles of the FPA films increased as the fluorine content of the PFA emulsion were increased. When placing the droplets on the coated filter paper, the WCAs were much higher than that on the polymer film. However, oil drop could completely wet the filter paper, which is due to the capillary effect of the porous structure of the filter paper. The oil-water separation efficiency reached a maximum, then decreased as the hydrophobicity and oleophilicity of the coated filter increased. This trend indicates that the oil-water separation efficiency reached a maximum state when the coated filter paper was in a suitable wetting state. The testing result shows that filter paper coated with sample F_4 FPA emulsion exhibited the highest oil-water separation efficiency and reached 94.45 wt%, which is only a little lower that the superhydrophobic and superoleophilic filter paper prepared in Wang's study (96.5 wt%) (Wang *et al*. 2010).

Mechanical Strengths of Filter Paper

The mechanical strengths of the pristine filter papers and coated filter papers (sample F_4) were tested, and the results are shown in Table 3.

Table 3. Mechanical Strengths of Filter Papers

Sample	Bursting strength (KPa)	Stiffness (15°, mN·m)	Tensile strength (KN/m)
Pristine filter paper	86	0.6	1.0
Coated filter paper	268	2.4	3.6
Coated filter paper wetted by diesel oil	232	2.1	3.0

Table 3 shows that the mechanical strength of pristine filter paper was greatly enhanced after being coated with the PFA emulsion, even when the coated filter paper was wetted by the diesel oil, it still maintained excellent mechanical strength, which indicates that the mechanical strength of the coated filter paper was strong enough for industrial application.

Surface Morphology

Figure 4 shows the geometric microstructures of the filter paper after the FPA emulsion (sample F_4) treatment. From Fig. 4, it is clear that the FPA emulsion coated the surface of the fiber without damaging the porous structure of the filter paper. However, the wettability of filter paper was transformed from superhydrophilic and superoleophilic to highly hydrophobic and superoleophilic. The pristine filter paper can be completely wetted by water droplets, which results from the existence of abundant hydroxyl groups and abundant cavities in the pristine filter paper structure. However, after treatment with the FPA (sample F_4) emulsion, the water cannot wet the filter paper, which is attributed to the hydrophobicity of the PFA coating. Therefore, the water droplet comes into contact with the trapping air due to the porous structure of the filter paper, increasing the water contact angle dramatically, which is consistent with the Cassie-Baxter theory (Cassie and Baxter 1944). Diesel oil can easily wet the coated fiber and therefore penetrate through the filter paper immediately. The treated filter paper is therefore suitable for separating water from oil.

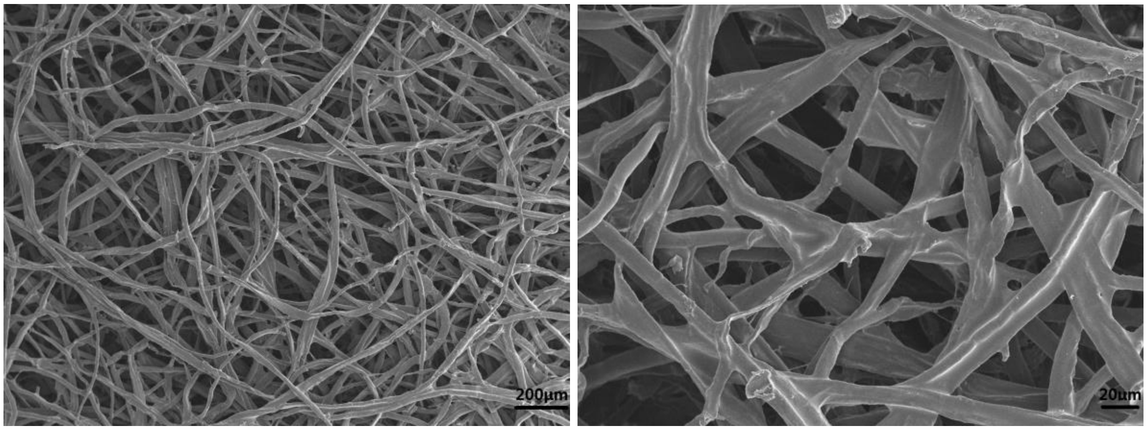

Fig. 4. SEM image of filter paper coated with FPA (sample F_4) emulsion

Long-term Stability of the Oil-Water Separation Properties

Many surfaces with superhydrophobic and superoleophilic properties based on micro-nano dual structures may be destroyed due to the flow of liquids passing through the filter material, and the destruction of the surface microstructure of a solid may lead to a change in CA, leading to a slow decline in the separation efficiency. In our experiment, the oil-water separation efficiency of the filter paper was studied 30 times with an interval time for each testing of 2 days. The testing results are shown in Fig. 5.

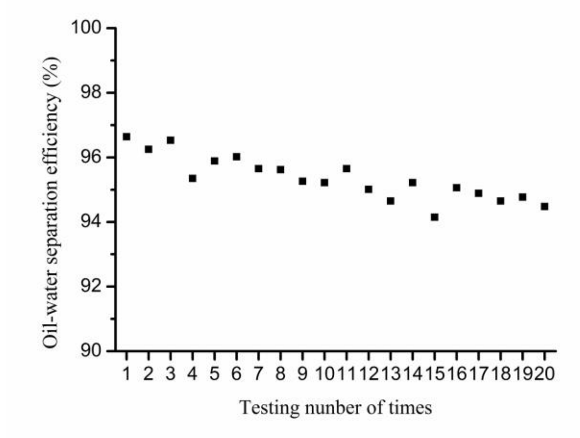

Fig. 5. Oil-water separation efficiency of filter paper *versus* testing times

As shown Fig. 5, the oil-water separation efficiency of filter paper was relatively steady over the course of 20 tests, demonstrating that the filter paper is suitable for industrial applications.

CONCLUSIONS

1. The wettability of filter paper was transformed from superhydrophilic and superoleophilic to superoleophilic and highly hydrophobic after coating with the PFA emulsion.

2. The highly hydrophobic and superoleophilic filter paper possesses excellent water-oil separation properties and strong mechanical strength, which indicates that oil-water filter paper can be fabricated via a simple and cost-effective coating route.
3. The coated filter paper showed an excellent oil-water separation efficiency stability after testing for 20 times. These properties indicate that the filter paper will have a considerable range of potential industrial applications.

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