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Effect of poly(ethylene oxide) and water on electrospun poly(vinylidene fluoride) nanofibers with enhanced mechanical properties as pre-filter for oil-in-water filtration

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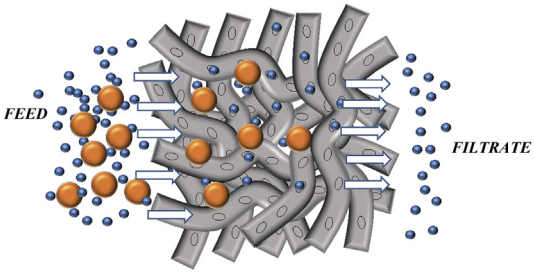
HIGHLIGHTS

- Porous PVDF nanofibers were successfully fabricated.
- Improvement in the mechanical properties of the porous PVDF nanofibers were achieved.
- The porous PVDF nanofibers possessed higher flux rate at 0.2 bar.

GRAPHICAL ABSTRACT



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ABSTRACT

Poly(vinylidene fluoride) (PVDF) nanofibers were fabricated by combined electrospinning and selective removal of poly(ethylene oxide) PEO from a PVDF/(PEO)/water (H_2O) composite. The method involved varying the concentration of PEO and H_2O with respect to PVDF and *N*,*N*-dimethylformamide (DMF) respectively. The morphology and other properties of the nanofibers were characterized by SEM, FT-IR, UTM, CFP and AFM and showed improved properties that can be effectively utilized as a pre-filter for pretreatment of oil-in-water emulsion filtration. The as-electrospun PVDF nanofiber films exhibited high flux rate, higher porosity, high Young's modulus and tensile strength, and high surface roughness. Results showed that the nanofiber films can achieve a flux rate of 1172 $Lm^{-2}\ h^{-1}$ with 96% filtration efficiency at a pressure as low as 0.2 bar in an oil-in-water emulsion system. The results indicate that these electrospun PVDF nanofiber films with high intra-pores can be used as a pre-filter in membrane filtration to reduce fouling on membranes. This will aid in cutting down cost since frequent cleaning of membranes shortens the membrane life span.

1. Introduction

Due to the growing concerns about the environmental issues that arise from the petroleum, oil refinery industries, food processing, lubricant, and metal finishing, there is a need for efficient

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treatment and separation of oil and water mixtures. Due to the small size of oil droplets in wastewater which is usually in the micrometer range, it's quite difficult to separate oil from oily wastewater [1]. In the past few decades, there have been numerous technologies and techniques developed to separate oil-water mixture, such as ultrasonication, biological treatment, electro-floatation, membranes, etc. [2–4]. Polymeric filtration membranes have been considered an advanced technology for separating oil-water mixtures [5]. But due to constant cleaning of the membranes as a result of fouling by oil droplets, the efficiency of the membranes decrease. Membranes used industrially for oil water filtration are costly and need to be used for their full designated lifespans. To improve the lifespans of membranes by preventing ease of fouling of the membranes, there is a need for a pre-filter which is of very low cost, high flux and efficient.

Polymeric nanofibers have attracted a great deal of attention in recent years as they find applications in areas such as filtration, textiles, drug delivery, polymer electrolyte, solid phase extraction, superhydrophobic materials, tissue engineering, energy, and environment [6–11]. The properties of nanofibers such as high porosity, highly interconnected pore structures, low density, high surface area to volume ratio, and good flexibility, make them applicable in the aforementioned areas [12–14]. Nanofibers have been fabricated by different processes such as self-assembly melt-blow, bicomponent spinning, flash spinning, phase separation, drawing, extrusion and electrospinning [15,16]. Among these fabricating procedures, electrospinning is found to be the most commonly used process because of its simplicity and versatility for producing polymer nanofibers [17].

The properties of nanofibers can be modified by introducing porous structure in the fibers. This creates more specific surface areas in the nanofibers and thus increases the overall surface area of the nanofibers as compared to the conventional electrospun nanofibers. Porous nanofibers have generated much interest in recent years due to their application in tissue engineering, solid catalyst, filtration and drug delivery. Porous structures in the nanofibers have significant influence in the final application of the electrospun nanofibers [18]. There are several ways of generating porous nanofibers such as selective dissolution, thermally induced phase separation (TIPS), and electrospinning of ternary system of non-solvent/solvent/polymer [19,20].

However, these methods used for generating porous nanofibers lack the mechanical properties possessed by the base polymer. Therefore, an inexpensive and versatile method of designing porous nanofibers that provides better mechanical properties is essential, especially for oil-in-water filtration. Poly(vinylidene difluoride) (PVDF) polymer possesses unique properties, such as high mechanical strength, superior chemical resistance, good thermal stability, and high hydrophobicity compared to other polymeric materials. Due to its outstanding properties, it has attracted much attention and has been one of the most used polymeric materials for forming microfiltration and ultrafiltration membranes, and energy harvesting [21–24]. Poly(ethylene oxide) (PEO), a thermoplastic, water soluble polymer was used as the porogen due to its ability for improving pore configurations [25]. PVDF and PEO blends have been well studied in the literature in the area of polymer electrolytes [26].

This study aims at employing electrospinning of non-solvent/solvent/polymer and selective removal to fabricate PVDF nanofiber by introducing nanopores on the fibers which led to improved mechanical properties and high flux of the nanofiber at 0.2 bar and room temperature. The nanofibers were then characterized and tested for oil-in-water filtration.

2. Materials and methods

2.1. Materials

Poly(vinylidene fluoride) (PVDF) was dried in the oven for 4 h before used. Poly(ethylene oxide) (PEO, Mw = 900,000) and *N*,*N*-dimethylformamide (DMF) were obtained from Acros (Geel, Belgium). All chemicals were used without further purification. Deionized (DI) water was use as the source of water throughout the experiment.

2.2. Preparation of PVDF nanofibers

The PVDF nanofibers with intra-pores were prepared by electrospinning and selective dissolution methods. The electrospun solutions were prepared by dissolving 10 wt% PVDF, PEO (with varying concentration), and water (with varying content) in DMF, and magnetically stirred at 60 °C for 12 h to obtain a homogenous solutions. The detailed information on the concentrations of various components in the electrospinning solutions is listed in Table 1. The obtained homogeneous solutions were then electrospun using a syringe and a needle with a tip-inside diameter of 0.25 mm, at a voltage of 15 kV, flow rate of 1.0 ml/h and a distance of 13 cm between the spinneret and the collector (aluminum foil). The electrospinning experiment was performed at room temperature of ~23 °C and relative humility of ~55%; this was chosen due to our preliminary experiments. The collected electrospun nanofiber mats were washed in a water bath at 60 °C for 1 h to remove the PEO and then the nanofiber mats were washed again with distilled water and acetone labelled accordingly (H1, H2, P2 and H3 nanofibers mat for the porous nanofiber mat with respect to varying PEO content and constant H_2O, P0, P1, P2 and P3 for porous nanofiber with respect to varying the concentration of H_2O with constant PEO concentration, NFPB for the composite nanofiber without wash and NF for the pure PVDF nanofiber mat), and then dried in a vacuum oven at 80 °C for 12 h.

2.3. Characterization

The morphologies of the electrospun nanofibers were characterized by scanning electron microscope (SEM) (JEOL JSM-5900, Japan), with an accelerating voltage of 20 kV under low vacuum. The nanofiber mats were evenly placed on a double sided carbon tape on aluminum stubs and sputter coated with a platinum-palladium mixture for 150 s for two conservative cycles at 13 mA and the nanofibers were observed from the SEM images. The IR spectra of the nanofibers were obtained with Fourier transform infrared spectroscopy (FT-IR) (Varian 2000) in the ATR mode with

Table 1
Concentrations of PEO (with respect to PVDF) and H_2O (with respect to DMF) used for nanofibers preparation, and contact angle of the nanofibers.

Sample	PEO (wt%)	Water (wt%)	Contact angle (°)
[a]NF	0	0	142.5 ± 0.5
[b]P0	7	0	147.0 ± 0.4
P1	7	1.1	151.4 ± 0.2
P2	7	2.2	156.5 ± 0.2
P3	7	3.3	148.7 ± 0.7
[c]H0	0	2.2	144.9 ± 0.5
H1	2	2.2	147.2 ± 0.2
H2	5	2.2	150.3 ± 0.7
H3	10	2.2	148.4 ± 0.6

[a] PVDF nanofiber.
[b] Porous nanofiber with varying H_2O content.
[c] Porous nanofiber with varying PEO content.