

Preparation of various nanofibrous composite membranes using wire electrospinning for oil-water separation

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Abstract

Due to growing demand for production of safe water a search of new materials for water purification is of critical issue. Their production should be of low cost and offers easily scalable manufacturing protocol. In this study, we have described preparation and properties of hydrophilic/oleophobic microfiltration membranes produced by means of wire electrospinning. Selective separation of oil or water was tested for oil-water emulsion by using a dead-end filtration unit. The obtained data allowed us to claim membranes as excellent separators for splitting emulsions.

Introduction

During the past decades, membrane separation has become an emerging technology for such industries as beverages, starch and sweetener, pharmaceutical, petrochemical, bulk chemical, water treatment, dairy and so on. The useful membrane processes are microfiltration, nanofiltration, ultrafiltration, reverse osmosis, forward osmosis, electrodialysis, and gas separation. The selection of a membrane is a key element for the optimum efficiency of the process. The membranes and the separation process should be selected based on the application area. For instance, a microfilter is one of the efficient material to separate oil droplets from oil-water emulsion [1–4]. It is characterized by permeate flux, that shows the amount of medium passing through membrane, and by selectivity describing preferential transportation of one compound over others.

Polypropylene (PP) nonwoven mats have been widely used in oil spill cleanup due to their oleophilic properties, good oil-water selectivity and easiness of fabrication. However, oil sorption capacity of PP nonwovens is limited due to large fiber diameters [5–7]. To bypass that obstacle nanofibers from polyvinylidene fluoride (PVDF) or polystyrene (PS) have been used frequently for oil-water separation [7, 8].

In this study, needle-free wire electrospinning system was used for the production of nanofiber webs. Polyacrylonitrile (PAN) and PVDF were selected for oil-water emulsion. PAN is highly polar and hydrophilic polymer while PVDF has hydrophobic character with high chemical resistance and excellent mechanical strength. In our previous work, it was found that PAN nanofibers had weak mechanical strength in comparison to PVDF [9]. Hence, we assumed that blends of PVDF and PAN should give nanofibers with better mechanical properties than neat PAN. To the best of our knowledge, only few works have reported improvement of strength [10, 11]. However, raising the mechanical strength did not fully characterize the searched microfilter. Hence, the second membrane metrics, their separation efficiency, had to be evaluated. In this study, we investigated nanofibrous



composite PVDF, PAN and PVDF/PAN membranes with a high specific surface area, directly prepared via wire electrospinning device without any post treatment, for the use as oil-water separators.

Materials and Methods

8% wt. polyacrylonitrile ($M_w=150$ kDa, purchased from Dicherma, China) was dissolved in dimethylformamide while 13% wt. polyvinylidene fluoride (donated from Kynar, France) was dissolved in dimethylacetamide. The solvents were purchased from Penta, s.r.o., Czech Republic. Solutions were mixed over the night at a temperature 50°C . The mixtures for electrospinning were prepared as shown in Table 1. Needle-free wire electrospinning device (Figure 1) was used for electrospun of nanofiber web under stable electrospinning conditions in a close chamber. All the samples were laminated with a 120 g/m^2 polyester spunbond nonwoven web to improve mechanical stability. The surface of the membranes was characterized by Scanning Electron Microscope (SEM, Vega 3SB) and fiber diameter were analyzed by Image-J program. An 1200-AEL capillary flow porometer (Porous Media Inc., Ithaca, NY) was used to measure the pore size and pore distribution.

Table 1. The code for each sample, the ratio of polymers, area weight and pore size of nanofibers.

Sample code	PVDF/PAN wt. ratio	Area weight	Pore size
P1	1/0	$3.52 \pm 0.5\text{ g/m}^2$	$2030 \pm 562\text{ nm}$
P2	0/1	$1.29 \pm 0.5\text{ g/m}^2$	$710 \pm 344\text{ nm}$
P3	2/1	$1.99 \pm 0.5\text{ g/m}^2$	$790 \pm 516\text{ nm}$
P4	1/1	$4.35 \pm 0.5\text{ g/m}^2$	$910 \pm 245\text{ nm}$
P5	1/2	$0.72 \pm 0.5\text{ g/m}^2$	$820 \pm 324\text{ nm}$

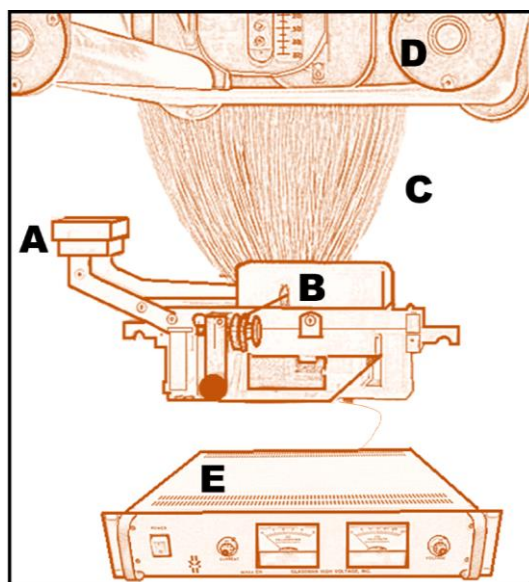


Figure 1. Schematic illustration of wire electrospinning device; (A) a solution tank feeds the solution toward the wire, (B) wire electrode, (C) spinning area, (D) take-up cylinder connected to supporting material, (E) high voltage supply.

An Amicon 8050 dead-end filtration cell was used for microfiltration test. Feed solution was prepared by mixing of distilled water/vegan oil with the volume ration of 1/1. Water was colored by methylene blue to observe the separation process properly. At the beginning of each filtration, 20 mL of distilled water was pumped throughout membrane. The cell was filled with 50 mL of emulsion and pressurized

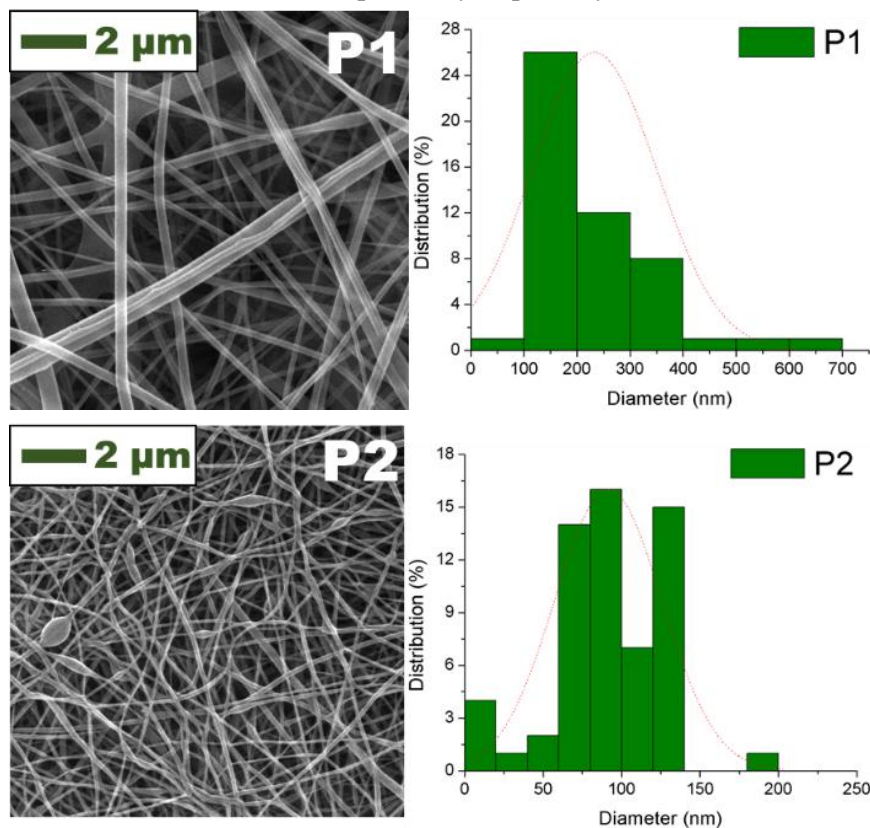
to 0.02 bar. For each test, 15 mL of permeate was collected. It was kept in a glass tube for 24 hours to determine water and oil volumes.

Results and Discussion

Surface Analysis and Characterization of Membranes

SEM images of the samples are shown as in Figure 2. The data revealed that PVDF nanofiber had almost 2.5 times larger diameter compared to PAN nanofibers. Mixing of PVDF with PAN decreases the diameter of the fibers nearly 1.6 times compared to neat PVDF fibers.

It is well-known that nanofiber diameter has an influence on the pore diameter of the nanofibrous membranes [12, 13]. Lowery suggested that there is a strong correlation between the diameters of fiber and pore of electrospun mats produced under the same conditions [14]. PVDF nanofibers have better mechanical properties compared to PAN nanofibers. Even a slight tension can easily damage the PAN material. On the other hand, PAN nanofiber web has lower fiber diameter and pore size compared to PVDF. Blending of these two polymers results in mechanical properties and pore size. It was found that mixture of PVDF and PAN increase improves hydrophilicity of the obtained material [9].



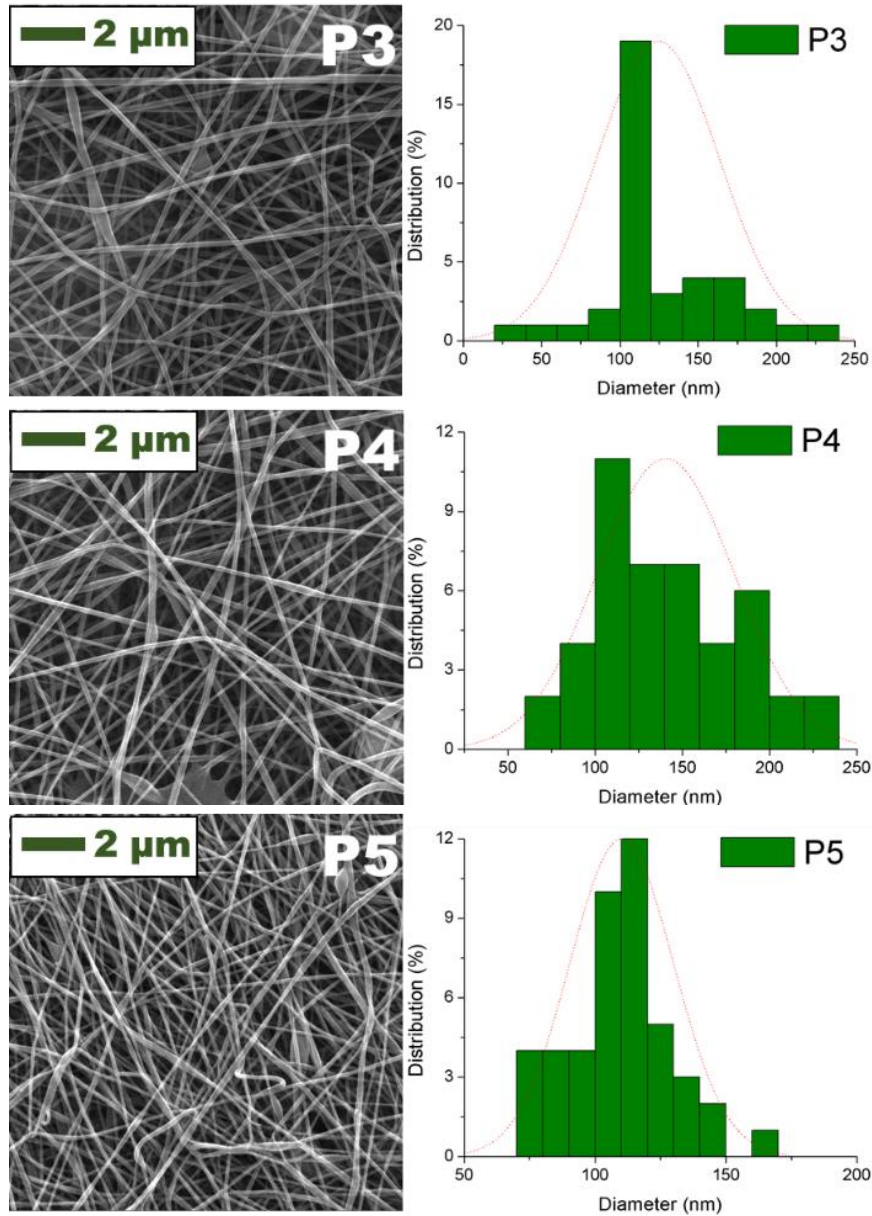


Figure 2. SEM images and fiber diameter distribution of nanofiber webs

Oil-Water Separation

Separation of oil-water emulsions is always difficult and some microfilters are used for that purpose. Nanofibrous membranes of PAN, PVDF and their blends were tested for oil-water separation. The permeate flux (F) and the permeability (k) of the membrane were calculated (Eq. (1) and (2)):

$$F = \frac{1}{A} \frac{dV}{dt} \quad \text{L/hm}^2 \quad (1)$$

$$k = F/P \quad \text{L/hm}^2\text{bar} \quad (2)$$

where A is the effective membrane area (m^2), V is the total volume of permeate (F), P is transmembrane pressure (bar), and t is the filtration time (h) [11].

The permeability of the membranes is shown in Figure 3.

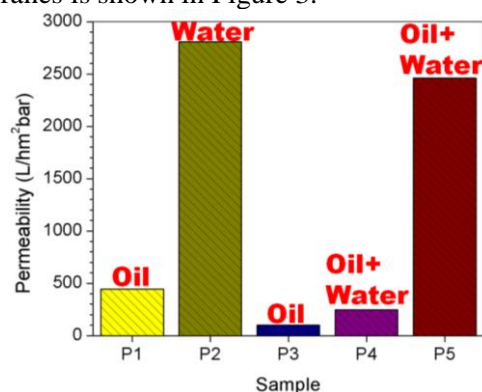


Figure 3. Oil-water permeability of the various nanofibrous membranes

It is well-known that PAN has a highly polar group which impart to the hydrophilicity of the membrane. The permeability test showed that PAN nanofibrous membranes have the highest permeability compared to other membranes. The permeability of the PVDF/PAN samples increased with the amount of PAN in the mixture. Oppositely, PVDF nanofibrous membrane selectively separate oil from the water; only oil passed through the PVDF membrane as the polymer had hydrophobic character. Its low surface energy (25 dynes cm^{-1}) generated membrane oleophilicity expressed in water contact angle of 158° and oil contact angle less than 1° [15].

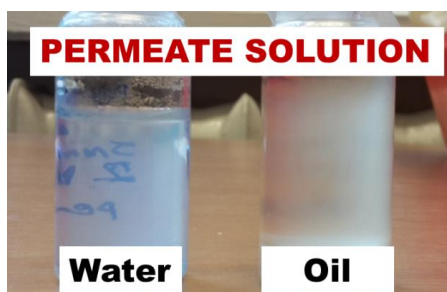


Figure 4. Permeate solution after separation of the oil-water emulsion.

The permeate solution was collected and kept for 24 hours to determine oil/water content (Figure 4). The results are listed in Table 2.

Table 2. Comparison of oil-water fraction of the permeate solution for various membranes.

Sample code	Polymer ratio (PVDF/PAN)	Oil/water ratio (%)
P1	1/0	100/0
P2	0/1	0/100
P3	2/1	100/0
P4	1/1	50/50
P5	1/2	27/73

The results showed that the PVDF nanofibrous membranes allowed oil to permeate mostly while PAN membranes induced water permeability. Moreover, the neat PAN membranes had higher permeability than other membranes. The oil-water permeability of the PVDF/PAN mixture depends on the fraction of polymer in the blend. Sample P5 showed oleophobic character while sample P3 was characterized

by oleophilicity. It pointed that PVDF affected the surface character of the prepared material. The oil content of permeate remarkably decreased by raising the amount of PAN in the polymer blend. These results indicated higher oil rejection could be achieved by using neat PAN. However, the neat PAN nanofibers are fragile and can be easily damaged. It seems to us that PVDF polymer could be added to PAN in lower ratio than 1/2 to strengthen the membrane stability. Evaluation of mechanical improvements will be subject of our future work.

Conclusion

In this work, we have developed nanofibrous composite membranes for oil-water separation without any post treatment. A facile, inexpensive method for the fabrication of nanofibrous webs was used. Two polymer PVDF and PAN was selected for electrospinning. Their blends affected the separation of oil-water emulsions. The neat PAN nanofibrous membranes showed the best water permeability while neat PVDF facilitated oil permeability. Significant achievements were made in study on the use of electrospun materials as microfilters for separation of oil-water emulsions. We believe that this kind of microfilters is a promising candidate for the use in the large-scale removal of oily aqueous streams. However, the additional studies on these membranes are needed to better understand their properties.

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