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Self-sustained electro-spun polysulfone nano-fibrous membranes and their surface modification by interfacial polymerization for micro- and ultra-filtration

P. Arribas [a,b], M. Khayet [b,c,*], M.C. García-Payo [b], L. Gil [d]

[a] Campus of International Excellence, Moncloa Campus (UCM-UPM), Madrid, Spain
[b] Department of Applied Physics I, Faculty of Physics, University Complutense of Madrid, Avda. Complutense s/n, 28040 Madrid, Spain
[c] Madrid Institute for Advanced Studies of Water (IMDEA Water Institute), Calle Punto Net N° 4, Alcalá de Henares, Madrid, 28805, Spain
[d] Genetics and Eco-Physiology Research Group, School of Forest Engineering, University Polytechnic of Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

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ABSTRACT

Polysulfone electro-spun nano-fibrous membranes (PSU ENMs) were prepared using a mixture of solvents *N*,*N*-dimethyl formamide (DMF) and tetrahydrofurane (THF) for microfiltration and ultrafiltration. The involved electro-spinning parameters, namely, the polymer solution flow rate, the electric voltage and the distance between the needle tip and the collector were varied in the range within which it was possible to obtain bead-free PSU ENMs. Their effects on the morphology and structure of the PSU ENMs were studied. Interfacial polymerization technique was applied to develop novel thin-film composite polyester-PSU based ENMs. The prepared membranes were characterized by means of different techniques such as scanning electron microscopy, contact angle measurements, X-ray diffraction, attenuated total reflectance Fourier transform spectroscopy. Micro/ultra-filtration tests were conducted using humic acid model solutions with a concentration of 15 mg/L at two different pH values (3 and 11). It was observed that PSU ENMs were not selective under acidic conditions, whereas the thin-film composite polyester-PSU based ENMs achieved better separation factors and lower irreversible fouling factors than those of the un-modified PSU ENMs.

1. Introduction

Electro-spinning is recognized as an efficient technique for the fabrication of polymer sub-micron to nano-scale fibers by applying electric forces. Electro-spun nano-fibrous membranes (ENMs) exhibit a great potential in membrane filtration technology due to several attractive attributes, such as their highly porous and interconnected pore structure, micron scaled interstitial space, controllable thickness and a large surface area to volume ratio [1,2]. These outstanding properties render ENMs to be one of the most cost-effective alternatives to successfully compete with conventional separation processes for the treatment of different types of wastewaters. Other advantages of using ENMs for wastewater treatment include high permeability and acceptable separation factor [3].

Among the used synthetic polymers for preparation of membranes for different separation processes, polysulfone (PSU) has been widely considered because of its excellent physicochemical properties (i.e. chemical resistance, thermal stability and mechanical strength as well as good processability). In general, PSU membranes have a broad operating temperature and pH ranges, excellent chlorine tolerance and ability to retain their mechanical properties in both hot and wet environments [4]. However, PSU membranes are not immune to fouling problem, which results in serious decline of permeate flux with changes of the separation characteristic during filtration operations. Various techniques such as surface coating, plasma treatment and surface grafting have been considered in order to overcome this drawback by improving the anti-fouling characteristics of the membrane and reducing therefore the foulant(s) adsorption to its surface [5].

The main purposes of the present study are the preparation and characterization of PSU ENMs using different electro-spinning parameter conditions. Attempts are made to prepare a thin-film composite (TFC) membrane by interfacial polymerization (IP) technique in order to improve the filtration performance of PSU

* Corresponding author at: Department of Applied Physics I, Faculty of Physics, University Complutense of Madrid, Avda. Complutense s/n, 28040 Madrid, Spain. Tel.: +34 91 3945185; fax: +34 91 3945191.
E-mail address: khayetm@fis.ucm.es (M. Khayet).

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ENMs. This technique is based on the polymerization that occurs between two reactive monomers at the interface of two immiscible solvents. The skin or thin layer produced by this technique will determine the overall solute retention, permeate flux and, in general, will control the efficiency of the membrane process. One of the advantages of the interfacial polymerization technique is that the thin layer can be optimized for particular function by varying the monomer concentration in each solution (both aqueous and organic solutions), the monomer ratios or the reaction time of the polymerization step [6].

2. Materials and methods

2.1. Materials

The spinning solution was prepared from the polymer polysulfone (PSU, UDEL P-3500 LCD, Solvay Specialty Polymers; Mw = 79,000 g/mol; $\rho = 1.24$ g/cm^3) and the mixture of solvents *N*,*N*-dimethyl formamide (DMF, Sigma–Aldrich) and tetrahydrofuran (THF, Sigma–Aldrich). The monomers bisphenol A (BPA, Sigma–Aldrich) and trimesoyl chloride (TMC, Sigma–Aldrich) along with the solvent hexane (Panreac) were used for the IP of the prepared PSU ENMs. Humic acid (HA, Fluka) of molecular weight 4.1 kDa was chosen as the model organic foulant. Hydrochloric acid (HCl, Sigma–Aldrich) and sodium hydroxide (NaOH, Panreac) were employed to adjust the pH of the feed humic acid solutions to the required values (3 or 11).

2.2. Preparation of PSU ENMs

Due to the possible influence of ambient humidity on PSU polymer, this was first dried at 120 °C overnight using a vacuum desiccator composed of a vacuum pump (Vacuubrand brand, model MZ2C), a desiccant (Afora) and a heating mantle (Selecta).

For the preparation of the polymer solution, DMF (64 wt.%) and THF (16 wt.%) were first mixed during 2 min at 80 rpm using a magnetic stirrer (IKA, RCT basic). Subsequently, 20 wt.% PSU was added to this mixture and the whole solution was stirred at 60 °C and 80 rpm during 15 h until the polymer solution becomes homogeneous.

Once the spinning solution was prepared, electro-spinning technique was used for the fabrication of the PSU ENMs. The electro-spinning set-up schematized in Fig. 1 consists of a glass syringe (50 mL, Nikepal) to hold the polymer solution, a circulation pump (KDS-200, Scientific) to control the polymer solution flow rate, two electrodes (a metallic Hamilton needle of 0.60/0.90 mm internal/external diameter and a grounded copper collector covered with aluminum foil to facilitate the extraction of the as electro-spun) and a DC voltage supply in the kV range (Iseg, TCIP300 304p).

The involved electro-spinning parameters (i.e. polymer solution flow rate, *F*; electric voltage, *V*; and distance between the needle tip and the collector or gap, *G*) were varied in the range within which it was possible to obtain bead free nano-fibers. These ranges were 1–3 mL/h, 16–20 kV and 10–15 cm, respectively. The electro-spinning time (t_e) was varied to obtain the desired thickness of the ENM. Furthermore, in order to increase the mechanical resistance and the structural integrity of the ENMs, a heat post-treatment was carried out at 220 °C for 2 h. It must be mentioned that the post-treatment temperature must be higher than the boiling point of the used solvents in order to ensure their complete evaporation from the formed ENMs. This temperature must be also above the glass transition temperature of the used polymer (185 °C for PSU) in order to form good contact and junction points between nano-fibers. Finally, the post-treated ENM was immersed in a bath containing distilled water for a short time to peel them out of the aluminum foil and subsequent drying at room temperature for 24 h.

2.3. Preparation of thin-film composite polyester-PSU based ENMs by interfacial polymerization (IP) technique

The prepared PSU ENM was first immersed in a 0.5 w/v% BPA aqueous solution for 15 min. Since the monomer BPA has very low solubility in water, it was dissolved in an aqueous solution of 2 M NaOH at basic pH. The soaked ENM taken out from the aqueous solution was positioned vertically for 2 min to drain the excess monomer on its surface [6]. Then, this ENM was dipped during 30 s in the organic solution prepared by mixing 0.15 w/v% TMC in hexane. The reaction of the monomers BPA and TMC occurs at the ENM surface forming a thin-film polyester layer of a few microns thickness. All these steps were carried out at ambient temperature, about 23 °C. Finally, the ENM was dried in air for 24 h before the characterization tests.

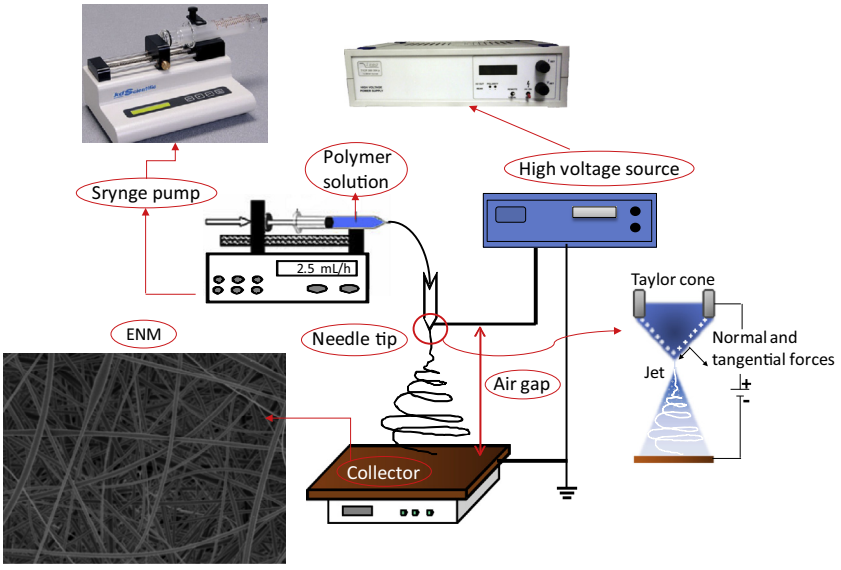

Fig. 1. Schematic diagram of electro-spinning set-up.