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TiO_2 entrapped nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties

Ahmad Rahimpour [a,*], Mohsen Jahanshahi [a], Babak Rajaeian [a], Mostafa Rahimnejad [b]

[a] Membrane Research Group, Nanotechnology Institute, Babol University of Technology, Iran
[b] Faculty of Chemical Engineering, Babol University of Technology, Iran

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ABSTRACT

In the current study, poly (vinylidene fluoride) (PVDF)/sulfonated polyethersulfone (SPES) blend membrane was modified using TiO_2 nano-particles. Firstly, sulfonation of polyethersulfone (PES) was carried out, then PVDF/SPES blend membranes were prepared with and without TiO_2 nano-particles in the casting solution using phase inversion induced by immersion precipitation technique. Polyvinylpirrolidone (PVP) with the concentration of 4 wt.% was added in the casting solution as pore former. The morphological studies were investigated using SEM, AFM, XRD, FTIR and contact angle goniometry. They showed that the average sizes of membrane pores in surface and sub-layer were reduced with addition of TiO_2 nano particles in the casting solution. The presence of TiO_2 nano-particles in the membrane structure was confirmed by XRD, FTIR and EDX analyses. The contact angle measurements demonstrated that the hydrophilicity of modified membranes was enhanced by addition of TiO_2 in the casting solution. The experimental results demonstrated that the initial flux of TiO_2 entrapped PVDF/SPES membranes was lower than the initial flux of neat PVDF/SPES membrane. The antifouling properties of membranes were improved by changing the membrane surface from hydrophobic to hydrophilic after TiO_2 addition in the casting solution. Finally, neat and 4% TiO_2 modified PVDF/SPES membranes were tested to possess the dramatic photo-bactericidal effect on *Escherichia coli* (*E. coli*).

1. Introduction

Phase inversion process has been widely adopted as a method for preparation of asymmetric polymeric ultrafiltration membrane [1–3]. Most of polymeric membranes used for micro- and ultrafiltration of liquids are prepared by phase inversion via immersion precipitation [4]. In this technique, a thin layer of polymer solution is immersed into a bath of non-solvent. At the same stage, precipitation (sometimes recognized as liquid–liquid demixing, phase inversion, crystallization) occurs leading to the formation of porous solid film. The structures of the formed membranes are very complex and dependent upon the composition of casting solution, coagulation bath [5–7]. Poly (vinylidene fluoride) (PVDF) is a semi-crystalline which shows outstanding thermal, chemical, and oxidation resistances against corrosive chemicals such as acids, bases, oxidants and halogens and exceptional hydrolytic stability. The crystalline phase of the polymer provides thermal stability while the amorphous phase accommodates the desired membrane flexibility and good mechanical and film-forming properties [8–11]. All the mentioned specifications make PVDF as an excellent polymer for microfiltration [12,13], ultrafiltration [14,15], pervaporation [16,17] and membrane distillation [18,19]. Moreover, the hydrophilicity and the pore structure of a membrane play key roles on the membrane separation performance. A suitable membrane must have high permeability, good hydrophilicity and a superior chemical resistance to the feed [20]. Due to hydrophobic nature of PVDF, many studies have been carried out on improving the PVDF membrane hydrophilicity and performance. These studies include physical blending, chemical grafting and surface modifying. Blending of polymers presents the advantage of an easy preparation by the method of phase inversion [11]. There are two different options for modifying the membrane formation; one process is addition of proper additive to the casting solution [21,22] and another is immobilization of polymers with hydrophilic segments by photo- or plasma polymerization [23–25]. One of the efficient methods to produce membranes with optimum morphology and specified properties is changing the composition in the dope solution or the coagulation bath. There are different surfactants [26], polymer [27], mineral fillers [28] and non-solvents [29], which can be used as additives. The role of the additives is to suppress and/or excite the formation of macro-voids, enhance pore formation and improve pore interconnectivity and/or hydrophilicity [30]. Sulfonated polymers were considered to be much more resistant to fouling [31,32]. The sulfonated polymers must be capable of forming asymmetric membranes with required

* Corresponding author. Tel.: +98 912 8093155; fax: +98 111 3220342.
E-mail addresses: ahmadrahimpour@nit.ac.ir, ahmadrahimpour@yahoo.com (A. Rahimpour).

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mechanical, thermal, chemical and separation properties. In a previous work [33], we prepared a modified PES membrane by blending of PES with SPES in the presence of polyvinylpirrolidone (PVP) as pore former in the casting solution. Results demonstrate that hydrophilicity, permeability, surface pore size and sub-layer porosity were significantly improved. Wang et al. [34] proved that the dispersion of inorganic particles in the polymer matrix have been useful in the improvement of membrane performance. There are many inorganic nano-particles which have been used to prepare polymeric membranes such as silica [35], Al_2O_3[36], Fe_3O_4[37], ZnO [38], ZrO_2[39], TiO_2[40–46], and CdS [47]. Nano titanium dioxide (TiO_2 nano-particles) as a nano-material improves the permeability and antifouling properties, so it has been the focus of numerous studies in recent years due to its innocuity, resistivity, photo catalytic and superhydrophilicity effects. Therefore, it has been applied to surface modification of several membranes [48,49].

Kim et al. [50,51] prepared a hybrid composite membrane by self-assembly of TiO_2 nanoparticles through interaction with the COOH functional group of an aromatic polyamide thin film layer. The membrane possessed significant photo-bactericidal effect on *Escherichia coli* under UV light illumination. Ebert et al. [52] discovered that PVDF and poly(amide-imide) (PAI) membranes blended with TiO_2 as inorganic filler had improved temperature resistance and permeability.

The main strategy of the present work was the preparation of PVDF membranes with high hydrophilicity. To obtain this goal at the first stage, the sulfonated polyethersulfone (SPES) was employed to blend with PVDF. Next step, TiO_2 nano-particles were used due to their potential reduction in antifouling abilities by changing parameters such as membrane topography and specially, hydrophilicity as well as self-cleaning properties. The sulfonation of PES was performed by sulforic acid (98%) as sulfonating agent. PVDF/SPES blend membranes were prepared with and without commercial nano-sized Titania by phase separation via immersion precipitation technique. The concentrations of TiO_2 nano-particles were 0.1, 0.5, 1, 2, 4 and 6 wt.% in the casting solution. The performance of prepared membranes was investigated by pure water flux, retention efficiency and flux of bovine serum albumin (BSA). The contact angles of the membranes were measured to evaluate the surface hydrophilicity. The surface and inner structures of the sample membranes were studied with several apparatus such as SEM, AFM and FTIR. X-ray diffraction was also employed to analyze the crystalline change of PVDF molecules. The antifouling and antibacterial properties of modified membranes with TiO_2 nano-particles were also investigated.

2. Experimental

2.1. Materials

Poly (vinylidene fluoride) (PVDF) from Alfa-Aesar as membrane polymer, polyethersulfone (PES Ultrason E6020P with M_w = 58,000 g/mol) and dimethylacetamide (DMAC) were supplied by BASF Aktiengesellschaft, Germany. Sulforic acid (98%) and polyvinylpyrrolidone (PVP, with M_w = 25,000 g/mol) from Merck were used. Titanium dioxide nanoparticles (TiO_2, particle size of 20 nm) and bovine serum albumin powder [some properties are followed: assay: >96%, mol wt: 66 kDa, pH ~7, solubility >40 mg/mL in H_2O] were obtained from Degussa and Sigma, respectively. Distilled water was used throughout this study.

2.2. Sulfonation of PES

Sulfonation of PES was performed by sulforic acid (98%) as sulfonating agent and solvent [33]. A glass reactor equipped with magnetic stirrer and condenser was charged with PES powder and sulforic acid (98%). The polymer dissolution time and temperature were 3 h and 20 °C, respectively. SPES was gradually precipitated into ice-cold distilled water under rapid stirring. The resulting precipitate was recovered by filtration and washing repeatedly with distilled water. Finally, the SPES was dried under vacuum at 40 °C overnight.

2.3. Preparation of PVDF membrane blended with the SPES and TiO_2 nano-particles

The flat sheet membranes were prepared by phase inversion via immersion precipitation technique. The blend homogeneous solutions based on PVDF and synthesized SPES polymers were prepared by dissolving two polymers at different concentrations of TiO_2 nanoparticles (0–6 wt.%) in DMAC as solvent in the presence of 4 wt.% PVP as pore former at around 25 °C with magnetic stirrer at 200 rpm for 8 h. The homogeneous polymer solution was kept for the removal of bubbles. The compositions of casting solution are shown in Table 1. The solution was sprinkled and cast using a home-made casting knife with 75 μm thickness on polyester non-woven fabric. This was immediately moved to the non-solvent bath for immersion at room temperature without any evaporation. The non-solvent was only water. The prepared membranes were washed and stored in water for at least 1 day to completely leach out the residual solvents and additives. As the final stage, the membranes were dried by placing between two sheets of filter paper for 24 h at room temperature.

2.4. Characterization of membranes

2.4.1. Contact angle measurement

In order to examine variations in the surface wetting characteristics of the PVDF/SPES membrane as a function of TiO_2 nanoparticle concentration, water contact angle was measured for membrane surface using a contact angle measuring instrument [G10, KRUSS, Germany]. This represents the membrane hydrophilicity. De-ionized water was used as the probe liquid in all measurements. To minimize the experimental error, the contact angles were measured at five random locations for each sample and the average number was reported.

2.4.2. FT-IR analysis

FTIR spectra of PVDF/SPES and PVDF/SPES/TiO_2 blend membranes were obtained for spectroscopic investigation. All FTIR spectra we recorded by the attenuated total reflection (ATR) technique using Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany) with horizontal ATR device (Ge, 45°). 32 scans were taken with 4 cm^{-1} resolution between 4000 and 500 cm^{-1}.

2.4.3. Morphological studies

In order to inspect the top surface and cross-section of membranes, SEM (Philips-X130) was employed. The membranes were cut into pieces of small sizes and cleaned with filter paper. These pieces were immersed in liquid nitrogen for 10–15 s and were frozen. Frozen bits of the membranes were broken and kept in air for drying. These dry samples were gold sputtered for producing electric conductivity, and

Table 1
Compositions of casting solution.

PVDF + SPES[a] (wt.%)	PVP (wt.%)	TiO_2 (wt.%)	DMAC (wt.%)
16	4	0	80
16	4	0.1	79.9
16	4	0.5	79.5
16	4	1	79
16	4	2	78
16	4	4	76
16	4	6	74

[a] 55% PVDF + 45% SPES.