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Preparation, characterization and performance enhancement of polysulfone ultrafiltration membrane using PBI as hydrophilic modifier

Erdal Eren*, Adem Sarihan, Bilge Eren, Huseyin Gumus, Fadime Ozdemir Kocak

Bilecik Seyh Edebali University, Faculty of Science and Arts, Department of Chemistry, 11210 Bilecik, Turkey

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ABSTRACT

In this study, new type of polysulfone (PSf) composite ultrafiltration membranes were prepared by blending PSf with poly[2,2'-(*m*-phenylene)-5,5'-dibenzimidazole] (PBI). The prepared membranes were characterized by water contact angle, SEM, FTIR, DSC, TG/DTG and cross-flow filtration techniques. We demonstrated that membrane characteristics such as porosity, hydrophilicity and thermal stability of PSf can be significantly enhanced with the incorporation of PBI. The composite membranes exhibited comparable bovine serum albumin (BSA) retention (69% vs. 36%) and water fluxes (355 vs. 228 L/m² h) against pristine PSf membranes.

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1. Introduction

Ultrafiltration (UF) membrane technology has vast applications in various industrial processes such as in food, pharmaceutical, biotechnological, pure water production and seawater desalination [1–4]. The hydrophilicity, porosity and surface roughness as well as mechanical strength of UF membrane plays an important role in membrane separation process [5]. Polysulfone (PSf) is widely used as a material for the UF membrane because of its excellent balance among the chemical and mechanical properties [6,7]. But, the use of PSf membranes is restricted due to its hydrophobicity. Hydrophobic properties of PSf membranes result in low water flux and serious membrane fouling caused by interactions with hydrophobic solutes. Therefore, different methods have been developed to obtain hydrophilic PSf membranes, such as blending with hydrophilic polymers [8–10], grafting with other polymers [11,12]. Due to its simplicity, polymer blending is an attractive technique for the design of new PSf membranes [8–10]. But, most of polymers form immiscible blends due to the effects of intermolecular interactions between unlike polymer pairs.

Poly[2,2'-(*m*-phenylene)-5,5'-dibenzimidazole] (PBI) has both proton donor (–NH–) and proton acceptor (–N=) hydrogen bonding sites. Due to the donor and acceptor hydrogen-bonding sites, PBI forms miscible blends with different polymers [13,14]. PBI is also known to absorb 15 mass% water at equilibrium and the

water in PBI is mobile [15]. These properties of PBI make it a promising membrane blending material for the UF applications. By using PBI additive in PSf, the various properties of PSf membrane such as hydrophilic–hydrophobic balance and morphology can be easily altered. These blend membranes can exhibit a better solute selectivity and water permeability in comparison to hydrophobic polysulfone due to the improvement in hydrophilicity.

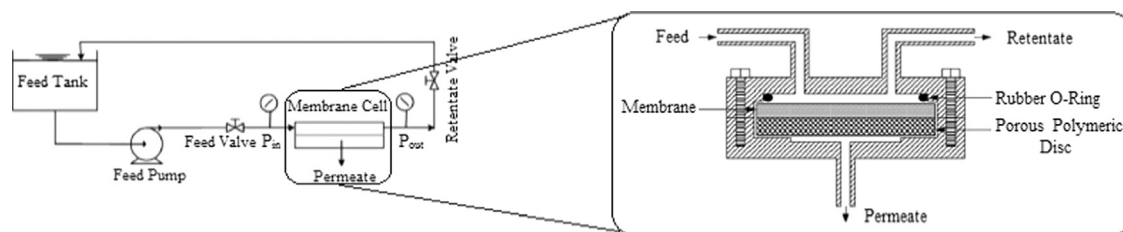
Although a lot of studies have been performed to modify the PSf membranes by addition of different additives, to our best knowledge there is no report about investigation of PBI addition effect on morphology and properties of PSf membranes. Therefore, the aim of this study is to examine the effect of PBI addition, a polybenzimidazole, into the casting solution for improving the performance of PSf membrane. In order to characterize the prepared membranes, water contact angle, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry (TG), derivative thermogravimetry (DTG) and

Table 1
Preparation conditions for polysulfone membranes.

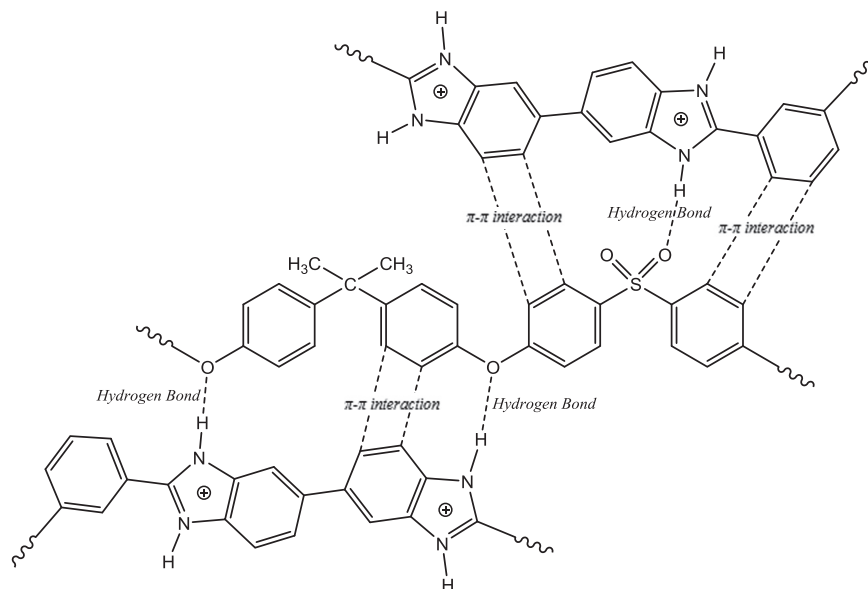
Membrane	Casting solution (wt%)			
	PSf	NMP	PEG 400	PBI
M0	17	73.00	10	0
M1	17	72.75	10	0.25
M2	17	72.50	10	0.50
M3	17	72.00	10	1.0

* Corresponding author. Tel.: +90 228 214 1480; fax: +90 228 214 1162.

E-mail address: erdal.eren@bilecik.edu.tr (E. Eren).



Scheme 1. Schematic diagram of the cross-flow filtration cell module.



Scheme 2. Possible H-bonding and π - π interactions between the functional groups of the PSf and PBI.

cross-flow filtration measurements were employed. The rejection performances of prepared PSf/PBI blend membranes were also determined using bovine serum albumin (BSA) as a model protein.

2. Experimental

2.1. Materials and instrumentation

PSf ($M_w = 22,000$ g/mol), *N*-methyl-2-pyrrolidone (NMP) and polyethylene glycol 400 (PEG-400) from Sigma-Aldrich Co. (USA) were used in the casting solution as the base polymer, the solvent and pore former, respectively. 3,3'-diaminobenzidine tetrahydrochloride ($\text{DAB} \cdot 4\text{HCl} \cdot 2\text{H}_2\text{O}$), polyphosphoric acid (PPA, 85% P_2O_5), isophthalic acid (IPA), and bicarbonate was purchased from Sigma-Aldrich Co. (USA). Bovine serum albumin (BSA, $M_w \sim 66$ kDa) was obtained from Bioshop, Canada.

The water contact angles for prepared membranes were determined at room temperature using sessile droplet method by a KSV Attension contact angle analyzer. At least five angles were measured for each sample and then the average value was calculated and reported. Exstar DSC 7020 differential scanning calorimeter was used to investigate the miscibility of polymers. A typical sample weight was about 5 mg and the scan speed was 20 °C/min under nitrogen atmosphere. FTIR spectra of the polymer were recorded in the region 3800 to 1000 cm^{-1} on a Spectrum-100 FTIR spectrometer. The TG and DTG curves were obtained using a Seiko Exstar 7200 thermal analyser under air atmosphere. The morphologies of membranes were examined by SEM (Carl Zeiss ULTRA Plus). The concentration of BSA was estimated with UV-vis spectrometer (PG instruments, T80) at $\lambda_{\text{max}} = 280$ nm wavelength.

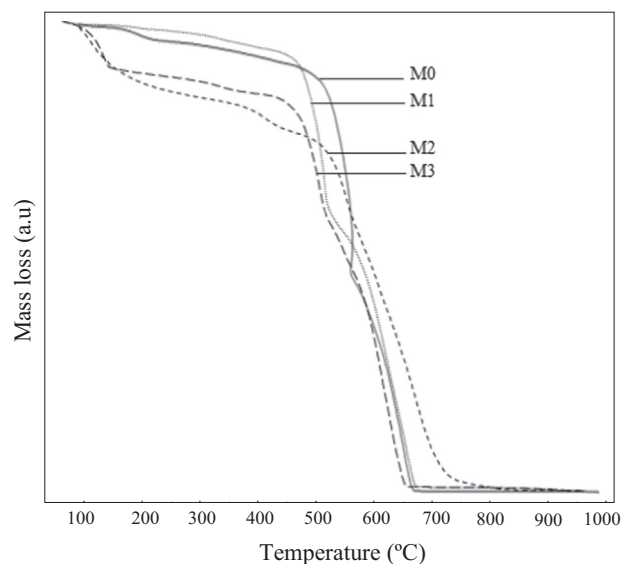


Fig. 1. TG curves of PSf and PSf/PBI blend membranes obtained at a heating rate of 10 °C min^{-1} in static air atmosphere.

2.2. Methods

2.2.1. Preparation of PBI

In a 500 mL round bottom flask equipped with a screw cap and a mechanical stirrer, $\text{DAB} \cdot 4\text{HCl} \cdot 2\text{H}_2\text{O}$ was gradually added to dissolve in PPA under nitrogen atmosphere at about 140 °C. After eliminating the hydrochloride, IPA was added into the solution and

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