Microporous and Mesoporous Materials 246 (2017) 24–36

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

A new high performance polyamide as an effective additive for modification of antifouling properties and morphology of asymmetric PES blend ultrafiltration membranes

Abbas Shockravi [a], [*], Vahid Vatanpour [a], Zahra Najjar [a], Saedeh Bahadori [a], Ali Javadi [b]

[a] Faculty of Chemistry, Kharazmi University, 15719-14911, Tehran, Iran
[b] Department of Polymer Engineering, The University of Akron, Akron, OH, 44325-0301, USA

ARTICLE INFO

Article history:
Received 16 July 2016
Received in revised form
25 September 2016
Accepted 13 March 2017
Available online 16 March 2017

Keywords:
Ultrafiltration
PES membranes
Polyamides
Fouling–resistance
Hydrophilic additive

ABSTRACT

Polyethersulfone (PES) ultrafiltration membrane with enhanced simultaneous permeability and fouling–resistance property was prepared using a new synthesized aromatic polyamide (PA-6) as an additive. A series of asymmetric membranes were prepared by adding different amounts of PA-6 to the casting solution using the phase inversion induced by immersion precipitation method. Attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR) and water contact angle measurement confirmed the PA-6 enrichment at the membrane surface and increased the membrane hydrophilicity and wettability. The SEM images elucidated the effect of PA-6 addition on the PES membrane morphology by increasing the pore density. The results of filtration performance, which carried out by dead-end filtration of bovine serum albumin (BSA) solution showed that the permeability and fouling resistance property was improved by optimizing the PA-6 content. When the PA-6 content was 2 wt%, the permeability reached approximately 10 times over the pure PES membrane. In comparison to the blend membrane of PES and 2 wt% of polyvinyl pyrrolidone (PVP), the blend membrane of 2 wt% of PA-6 showed significant flux recovery ability. The rejection of all the blended membranes was approximately at high point over 95%. In addition, the results were compared with those obtained using PVP as a usual additive. Although the PVP blended membranes exhibited higher permeability, they showed lower antifouling properties. Finally, a membrane with 1 wt% PVP and 1 wt% PA-6 was prepared and showed the best performance regarding improved permeability and antifouling properties.

1. Introduction

Membranes and membrane processes are not a novel invention. They have been involved in our daily life and exist as long as life exists. The preparation of synthetic membranes and their use in the large industrial scales, however, are the most recent developments which have rapidly achieved a substantial importance due to their practical applications. In fact, intrinsic characteristics of efficiency, operational simplicity and flexibility, relatively high selectivity and permeability for the transport of specific components, good stability under a wide spectrum of operating conditions, easy control and scale–up have made these systems useful in a variety of applications and operations. Molecular separation, fractionation, concentration, purification, clarification, emulsification, crystallization, etc., in both liquid and gas phases and in a wide spectrum of operating parameters such as pH, temperature, and pressure are considered as some of these applications [1].

In recent years, the synthetic polymeric membranes have been used for a wide variety of liquid separations such as nanofiltration, reverse osmosis, ultrafiltration (UF) and microfiltration. The UF membrane technology has found growing applications in various industrial processes such as food, paper, chemical, pharmaceutical, biotechnological, wastewater purification, and seawater desalination to retain desirable and undesirable water components including proteins, viruses, colloids, and pathogens [2–7].

Among different polymeric membranes, polysulfone (PSf) and polyethersulfone (PES) membranes have been extensively utilized in protein separation and purification because of their high thermal resistance, excellent hydrolytic stability, and ability to retain

---

[*] Corresponding author.
E-mail addresses: abbas_shockravi@yahoo.co.uk, shockravi@khu.ac.ir (A. Shockravi).

http://dx.doi.org/10.1016/j.micromeso.2017.03.013
1387-1811/

mechanical properties in hot and wet environments. In comparison with PSf, the PES generally exhibits higher hydrophilicity, which can increase the permeation and antifouling properties of the UF membranes. However, the inherent hydrophobic characteristics of PES which lead to hydrophobic interactions between membrane and solute in feed solution, the nonspecific protein adsorptions on the membrane surface and in the membrane pores, result in serious membrane fouling and deteriorate the permeation flux. This is an important issue in membrane filtration technology, resulting in a higher energy demand, shorter membrane lifetime, and unpredictable separation performance [8,9].

Hence, several methods have been used to increase the hydrophilicity of PES membrane surfaces to reduce fouling. A good technique is the modification of common polymers or membranes, such as PES and PES-based membranes to increase the antifouling property, biocompatibility, and other specific functions. Thus, introduction of hydrophilic functional groups and modification of polymers, through three common approaches such as surface grafting [10], coating [11,12], and blending with nanoparticles [13–16] or hydrophilic polymers [17–19] have been reported in the literature to improve the fouling-resistance and permeation property of PES membranes.

Blending of a hydrophilic polymer with the membrane-forming hydrophobic polymer seems to be an effective method to obtain the hydrophilic properties in UF-PES membranes. Among many hydrophilic polymers, those containing polyamides have been proved to be extremely effective in reducing protein adsorption [20,21]. In fact, polyamides are the most commonly used materials for the preparation of membranes because of their low pressure requirements, flexible operating conditions, and oxidant (chlorine, chloramine, bromine, ozone etc.) intolerant [22]. It is also noteworthy that the surface of a polyamide membrane carries an anionic charge which makes it suitable against filtration of protein solutions containing anionic charges. Nevertheless, most polymer blends are immiscible due to their small increase of entropy on mixing as well as the endothermic heat of mixing. The application of immiscible blends in many cases has been restricted because their poor interfacial properties [23]. For example, poly(1-vinylpyrrolidone) (PVP), as a non-toxic material is well soluble in water. Although PVP does not form miscible blends with PES, it has been widely examined for the preparation of UF membranes via the phase inversion method [24,25]. In phase inversion process, the PVP is dissolved by water (as a non-solvent) and the sites where PVP exists are converted to micropores. Since the PVP is water-soluble, most of PVP is washed out throughout membrane formation and only a small portion of PVP remains in the pore wall or the membrane matrix [26–28], resulting in the deteriorated antifouling properties. In addition, remained hydrophilic polymer in the membrane pore wall, surface, or matrix is critical in order to prepare membranes showing better hydrophilic characteristics.

The current study reports the fabrication and performance investigation of asymmetric PES membranes directly blended with a synthesized polyamide (PA-6) as a new hydrophilic polymer by the phase inversion method. The PA-6 was synthesized from biphenyl-2,2′-dicarboxylic acid and a recently developed diamine (DA) monomer in our laboratory [29]. The presence of flexible thioether linkage, non-coplanar thiazole units, and bulky pendant naphthyl rings imparted excellent solubility to the resulting PA-6. In order to keep hydrophilic polymer in the membrane matrix, water solubility of the hydrophilic polymer was controlled by the introduction of bulky phenyl and naphthyl groups in the polymer backbone. Moreover, pendant naphthyl groups and hydrophilic functional groups in the PA-6 backbone could obviously increase the permeability and hydrophilicity of the PES membranes. The effects of different amounts of PA-6 on the UF-PES membrane performance, morphology, and hydrophilicity of PES membranes were evaluated. The performances and the antifouling behavior of the fabricated membranes were investigated by measuring the permeability of pure water, flux decrease ratio, and bovine serum albumin (BSA) rejections as the obstructive model of PES/PA-6 blend membranes.

2. Experimental

2.1. Materials

The novel diamine of 5,5’-thiobis(2-amino-4-(2-naphthyl)thiazole) (DA) was prepared according to the reported procedure [29]. The aromatic dicarboxylic acid biphenyl-2,2′-dicarboxylic acid (MERCK) was used as received. *N*-methyl-2-pyrrolidone (NMP, MERCK) as polymerization solvent and pyridine (Py, Fluka) were purified by distillation under reduced pressure over calcium hydride (CaH_2) and stored over 4 Å molecular sieves prior to use. Lithium chloride (LiCl, MERCK) was dried at 200 °C for 24 h under vacuum before use. Triphenyl phosphite (TPP, MERCK) were used without further purification. PES with $M_w = 58{,}000$ g/mol was purchased from BASF company, Germany. Polyvinyl pyrrolidone (PVP) with $M_w = 25{,}000$ g/mol (PVP K30), 2-propanol for porosity evaluation, and bovine serum albumin (BSA) powder were obtained from Merck. Dimethylacetamide (DMAc) (Merck) was used as solvent. Distilled water was also used during this study.

2.2. Preparation of PA-6 as hydrophilic agent

PA-6 was prepared from DA and biphenyl-2,2′-dicarboxylic acid via Yamazaki polycondensation reaction based on our reported procedure (Fig. 1) [29]. This procedure described briefly as follow:

A mixture of 0.482 g (1 mmol) of DA, 0.242 g (1 mmol) of biphenyl-2,2′-dicarboxylic acid, 0.3 g of LiCl, 0.6 mL of triphenyl phosphite (TPP), 0.6 mL of pyridine, and 2 mL of dried NMP was heated and stirred at 120 °C for 6 h, under nitrogen atmosphere. At the end of the polymerization reaction, the PA solution was slowly poured into 300 mL of methanol under vigorous stirring. The resulting fibrous precipitate was filtered off, washed with hot water (2 × 100 mL) and hot methanol (100 mL) thoroughly, and dried in a vacuum oven at 100 °C overnight.

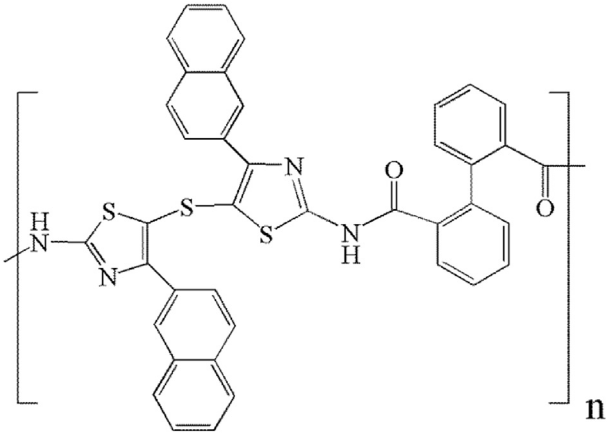

Fig. 1. Structure of the prepared PA-6.