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Polyethylene glycol cross-linked sulfonated polyethersulfone based filtration membranes with improved antifouling tendency



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ABSTRACT

Highly hydrophilic and fouling resistant porous membranes were prepared by covalent cross-linking of sulfonated polyethersulfone with amino terminated polyethylene glycol. Polyether sulfone (PES) was sulfonated and cross-linked with poly(ethylene glycol) bis-(3-aminopropyl) terminated via sulfonamide linkage using 1,1'-carbonyldiimidazole (CDI). The characteristics, the stability, and the separation performance of the prepared cross-linked membranes were evaluated in detail. The membranes were characterized with respect to membrane chemistry (by ATR-FTIR spectroscopy), hydrophilicity and surface energy (by dynamic contact angle), surface morphology (by scanning electron microscopy), pure water permeability, and rejection of bovine serum albumin (BSA) protein. The antifouling properties of the prepared membranes were assessed by protein adsorption and bacterial cell adhesion study. The cross-linked membranes exhibited superior water permeation, rejection, and antifouling performance to the neat membrane. The protein adsorption on membrane surface was about 10-fold less than that of the PES membrane. The results reveal that, hydrophilicity was increased due to PEG, leading to the 3-fold increase in water flux and more than 90% protein rejection efficiency.

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1. Introduction

Water contamination is a serious world-wide problem, and there is an urgent need for secure and sustainable source of water [1,2]. Membrane based water desalination/purification technologies have a wide range of advantages in comparison with traditional separation methods [3–5]. Membrane technology is widely applied for water treatment and receives significant attention because it is an outstanding process for the removal of particles, turbidity and microorganisms from water. The decay of membrane performance in many separation applications, such as water reclamation and desalination, due to biofouling arising from protein and natural organic matter adsorption and biofilm formation is of great concern because of the significant reduction in system productivity and increase in system operational cost [6].

For the development of ultra-filter (UF) membranes, a wide range of polymeric materials such as polyimide, cellulose acetate, poly ether ketones, polyether sulfones, etc. are being studied in an effort to improve membrane performance [7]. However, the membranes prepared using these polymeric materials suffer with variety of problems such as stability, hydrophobicity, fouling etc.

Organic and biological fouling are the most important problems for current membranes which are related to the membrane surface nature. Polysulfone/polyethersulfone (PES) is one of the most widely used materials in the manufacture of polymeric membranes due to its excellent mechanical strength, compaction-resistance, chemical stability, thermal resistance and its application in a wide pH (2–12) range. However, despite these benefits, its relatively hydrophobic nature is a considerable limitation in water filtration application because it does not allow water permeation at a significant rate and also prone to high degree of fouling. Therefore, the chemical structure of polysulfone must be altered to induce controlled levels of hydrophilicity, to enable high rates of water transport while maintaining good rejection, and to retain the excellent physical properties of polysulfone. Sulfonation and amination have been reported as materials' design strategies for increasing the hydrophilicity of polysulfone membranes [8,9]. In particular, sulfonated polysulfones have attracted great interest, because they have promising property profiles for desalination as they exhibit selective ion transport and are highly tolerant to aqueous chlorine over a broad range of pH values [10–12]. Hydrophilicity enhancements have also been achieved by various physical and chemical surface treatment procedures on preformed PES membranes or by doping the casting solution of the membranes with additives. Additives used in the fabrication of PES membranes can be broadly categorized into the polymeric additive groups of polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG),

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and weak solvents such as glycerol. The addition of PVP and PEG has become a standard method to obtain “hydrophilized” membranes [13]. In blended membranes, leaching out of hydrophilic additives from hydrophobic PES matrix leads to the deterioration of membrane performance. To avoid this problem, covalent grafting and cross-linking with additives have been suggested [14,15]. Several reports are available where covalent modification strategy is used to modify the PES based membranes for various applications [16]. Thermal induced graft polymerization is a facile method to modify PES membranes in presence of a chemical initiator or cleavage agent. Plasma induced grafting and polymerization of vinyl monomers on PES membranes is also reported to achieve highly hydrophilic surfaces and immobilization of biomolecules [17]. Covalent grafting via UV irradiation is mostly used to immobilize suitable hydrophilic molecules [18–20]. Surface grafting using gamma-irradiation is also reported, but the process leads to PES degradation [21]. In grafting method of modification, surface-initiated atom transfer radical polymerization has been widely used to prepare special surface material, since it is a “living” polymerization method that has been utilized for grafting polymers onto surfaces in a controlled manner, including graft density, chain length, and chemical composition [22]. Bulk modification of PES is also reported by grafting of suitable polymers via substitution and condensation reactions [14,23]. PES-g-PEG copolymer films synthesized through nucleophilic substitution on $-\text{CH}_2\text{Cl}$, exhibited high resistance to protein adsorption and cell attachment [14]. Modification of PES membranes with different functional groups by reacting chlorosulfonic acid group with different amine containing compounds reveals feasibility for covalent modifications via sulfonamide linkage [23]. Thus, in general, post modification of PES membranes are studied more in comparison to the modification at molecular level in bulk solution. The modification in bulk solution can be a specific approach for improving characteristics during membrane synthesis. Also, the leaching out of hydrophilic components from the membrane matrix can be avoided in covalently cross-linked membrane, which is a common problem in blended or surface coated membranes.

Herein we present the preparation of highly antifouling UF membranes by covalent cross-linking of amino functionalized PEG molecules via sulfonamide linkage for water purification and separation processes. The membranes were prepared by using sulfonated polyether sulfone because of its low cost, good film forming capability, and ease of controlled degree of functionalization. An overall membrane characterization was carried out to determine the effect of PEG cross-linking on the physico-chemical properties of the membranes, such as hydrophilic character, stability, permeability, and fouling resistance. In addition, the membrane performance during filtration of aqueous solutions containing BSA protein was studied for membrane permeability and solute rejection.

2. Experimental section

2.1. Materials

Polyethersulfone (PES, Ultrason E6020P, CAS no. 25608-63-3, $M_n=52,000$ g/mol, and the repetitive unit is shown in Fig. 1) was purchased from BASF. 1,1'-carbonyldiimidazole (CDI), poly(ethylene glycol) bis-(3-aminopropyl) terminated (PEG-NH₂, $M_n=1500$), bovine serum albumin (BSA), FITC-conjugated Albumin Bovine (FITC-BSA) and all other chemicals were obtained from Sigma-Aldrich Chemicals and used as received. Highly polished single crystal silicon wafers of {100} orientation with ca. 1.5 nm thick native silicon oxide layers were purchased from

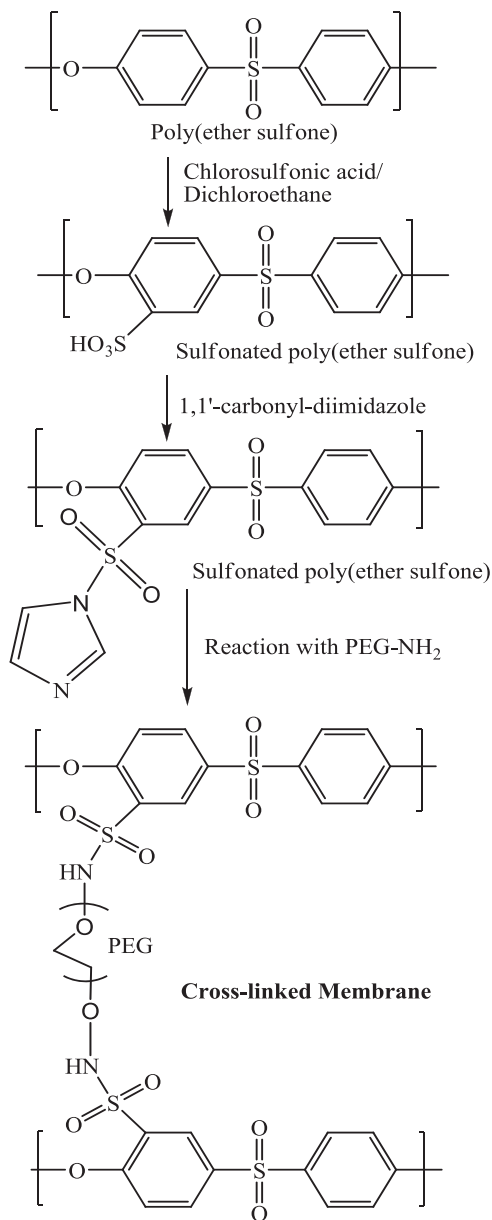


Fig. 1. Reaction scheme showing membrane preparation methodology and mechanism of PEG cross-linking.

Semiconductor Processing Co. and used as substrate for spin coating. Nonwoven polyester fabric support for the membrane preparation was kindly provided by Freudenberg Filtration Technologies, Germany. Deionized (DI) water and water purified with a Milli-Q system (Millipore) were used in this study.

2.2. Sulfonation and membrane preparation

The sulfonation of PES was carried out by direct electrophilic substitution reaction using chlorosulfonic acid as sulfonating agent [24]. For the reaction, the PES was first dissolved in dichloroethane (DCE) to obtain a 7.5 wt% solution. Similarly, a solution of chlorosulfonic acid diluted in DCE (10 wt%) was prepared. Then, chlorosulfonic acid solution was added drop-wise to the solution under the vigorously stirring over 3 h. The reaction was continued for another 6 h. After the reaction, the polymer was precipitated with at least a 5-fold volume of ice cold deionized water and washed with water until the last trace of acidity was removed. Thus obtained sulfonated polyethersulfone (SPES) was vacuum

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