



Formation of disulfonated poly(arylene ether sulfone) thin film desalination membranes plasticized with poly(ethylene glycol) by solvent-free melt extrusion



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ABSTRACT

In this study, we discuss a new membrane formation route for preparing sulfonated polysulfone desalination membranes by solvent-free melt processing. Single-layer membranes composed of a 20 mol% disulfonated poly(arylene ether sulfone) random copolymer (BPS-20K) and poly(ethylene glycol) (PEG) plasticizers were successfully prepared by using melt extrusion. The chemical integrity of the components in the BPS-20K/PEG membranes was maintained after the extrusion process, as confirmed by ¹H NMR and FT-IR analysis. Although some of the films appeared opaque after extrusion, this was found to be due to surface roughness. Other factors that might lead to film opacity, such as phase separation, crystallization, or micro-voids, were not found.

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1. Introduction

Most ionomer membranes used for water purification [1–3] and power generation [4,5], are prepared by solution processing using large volumes of toxic solvents [1,6]. For example, currently widely used reverse osmosis desalination membranes, i.e., polyamide (PA) thin film composite membranes, are obtained at a solvent/water interface via interfacial polymerization [1,2]. Such conventional polymer membrane formation methods are environmentally unfriendly, and the cost associated with waste disposal is high. There is a clear need to prepare ionomer membranes in a more environmentally and cost effective manner.

Sulfonated aromatic hydrocarbons have been studied extensively as membrane materials for such future energy applications as fuel cells, reverse electrodialysis, and redox flow batteries. They are competitive with existing commercial perfluorosulfonated polymer membranes (e.g., Nafion[®]) due to their low cost, simple chemistry, and excellent physical properties. In particular, sulfonated polysulfones have been investigated as candidate materials for reverse osmosis desalination [7–11] and fuel cell applications [5,12–16] because of their excellent thermal and mechanical stabilities, as well as good selective ion transport properties [5,7–16]. Furthermore, sulfonated polysulfone membranes may be prepared by solvent-free melt processing with an adequate plasticizer [17–24]. In principle, the glass transition temperature (T_g) and viscosity of sulfonated polysulfone are high because of the presence of sulfonate groups in the polymer matrix [10,25], and, thus, the melt processing of sulfonated polysulfones is difficult [26,27]. However, a suitable plasticizer, for instance poly(ethylene glycol), has been explored to lower the T_g and viscosity of sulfonated polysulfones

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and thus enable the melt processing of such materials [17,18,23,24,28]. After melt processing, the plasticizer can be removed by water extraction before use [28,29]. In this research, we study this new membrane formation path to prepare sulfonated polysulfone desalination membranes by solvent-free melt processing.

Earlier, Bebin et al. explored the possibility of extruding proton exchange membranes for fuel cell applications (PEMFC) using post-sulfonated polysulfone [23,24]. Several properties, such as proton conductivity and life span of extruded membranes, were reported; the extruded membranes showed decreased proton conductivity but increased life span compared to those of solution processed membranes. In addition, Sanchez et al. also prepared post-sulfonated polysulfone membranes for PEMFC applications by extrusion [19–21,30,31], investigated several candidate plasticizers for sulfonated polysulfones, and evaluated their rheological properties. However, previous work mainly focused on fuel cell applications, and to date no investigation has addressed the potential formation of desalination membranes by melt extrusion.

Additionally, the currently widely used membranes—i.e., polyamide (PA) membrane—for desalination have a thin film composite structure [1,6], and similar composite structures may be obtained by employing a coextrusion process with proper support layer materials [32–34]. The thin film composite structure consists of a very thin, selective layer (in this work, sulfonated polysulfone), and a porous support layer. The thin selective layer offers high selectivity of salt, and the porous support layer provides mechanical stability while preserving high water flux. Polypropylene (PP) could be used as a candidate support material to form a composite structure, since desirable porosity in PP can be achieved by various methods, including post-coextrusion stretching [32,35,36].

In this work, disulfonated poly(arylene ether sulfone)s (BPS) random copolymers have been explored for desalination membrane materials, and poly(ethylene glycol), PEG, oligomers were selected as plasticizers to enable melt extrusion of the BPS polymers. In previous studies, we reported the effect of PEG oligomers on the T_g and viscosity of BPS/PEG blends and found the potential compositions of BPS/PEG blends that were rheologically matched with PP to form a composite structure [17,18]. Using this information, single layer films of BPS-20K/PEG blends were prepared.

Thin films of 20 mol% disulfonated poly(arylene ether sulfone) random copolymer (BPS-20K)/PEG blends with uniform thickness (20–40 μm) were produced by melt extrusion. It was of interest to determine whether chemical structure and morphologies of extruded films are comparable to those of solution cast films. The molecular structure and composition (i.e., PEG \bar{M}_n , and concentration) in the extruded films were examined using Proton Nuclear Magnetic Resonance (^1H NMR) and Fourier Transform Infrared Spectroscopy (FT-IR) analysis to detect any thermal degradation during melt extrusion. Some extruded films were rather opaque compared to transparent solution cast films, and the origin of this opacity was investigated. The factors leading to film opacity such as micro-voids, phase separation, or excessive crystallization were examined with Scanning Electron Microscopy (SEM), gas

permeability measurements, and Differential Scanning Calorimetry (DSC). While the focus of this study is membrane formation, subsequent papers will report the PEG extraction kinetics from the extruded BPS-20K/PEG films, as well as the water and salt transport properties of the resulting pure BPS-20K membranes.

2. Materials And Experimental

2.1. Materials

2.1.1. Polymer: 20 mol% disulfonated poly(arylene ether sulfone) (BPS-20K)

Fig. 1 shows the chemical structure of the disulfonated poly(arylene ether sulfone) random copolymer (BPS) used in this study. BPS polymers were synthesized directly from sulfonated monomers as established by McGrath and others [9,10,17,37–39]. Nomenclature for this polymer is BPS-XY, where X is the molar percentage (mol%) of disulfonated monomer and Y indicates the cation forms in sulfonated groups, either H (acid form) or K (potassium form). For example, BPS-20K is in K (potassium) sulfonated form containing 20 mol% of sulfonated polysulfone segments and 80 mol% of non-sulfonated polysulfone segments.

The 20 mol% disulfonated poly(arylene ether sulfone) random copolymer, BPS-20K, has an ion exchange capacity (IEC) of 0.92 meq/g and was selected for its thermal and mechanical stability, as well as its selective ion transport properties [7,10,11,17]. BPS-20K polymer synthesized by Akron Polymer Systems (Akron, OH) was used as received. Table 1 provides the characteristics of the BPS-20K polymer.

2.1.2. Plasticizer: Poly(ethylene glycol) 200–400 g/mol

Poly(ethylene glycol), PEG, oligomers with molecular weight (\bar{M}_n) ranging between 200 g/mol and 400 g/mol were used as plasticizers for BPS-20K polymer [17,18]. Glass transition temperatures (T_g) and melting points (T_m) of PEG oligomers are summarized in Table 2. PEG concentration (wt%) in the melt extruded membranes ranged between 20 wt% and 30 wt%. The PEG oligomers were purchased from Sigma Aldrich (St. Louis, MO) and were used as received. Product information is as follows: PEG 200 Cat# P3015, PEG 300 Cat# 202371, and PEG 400 Cat# 202398.

2.2. Experimental

2.2.1. Sample preparation

2.2.1.1. Melt extrusion.

Single layer, extruded films of BPS-20K/PEG blends were prepared by a 5 ml twin screw micro-compounder with an attached heated film die (width = 65 mm) and film take-up system (DSM Xplore, The Netherlands). The desired amount of BPS-20K and PEG were weighed and carefully mixed before feeding to the micro-compounder. The micro-compounder was operated under an extra dry nitrogen atmosphere (99.9%, Matheson Tri-Gas, Austin, TX) to prevent polymer degradation. The processing temperature was selected to be 50–100 $^\circ\text{C}$ higher than the blend T_g and lower than the degradation temperature, T_d , as reported previously

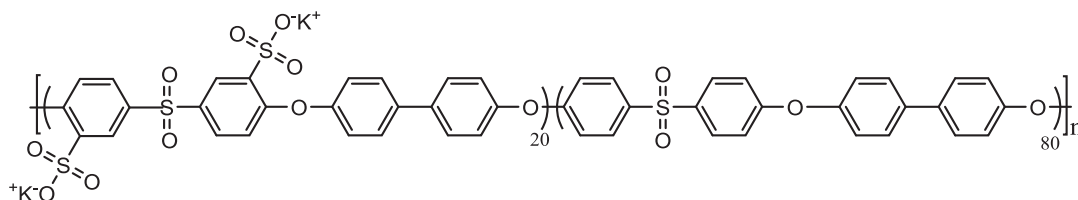


Fig. 1. Chemical structure of 20 mol% disulfonated poly(arylene ether sulfone) random copolymer (BPS-20K).

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