Polymer 55 (2014) 1574–1582

Contents lists available at ScienceDirect

Polymer

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

Rheological studies of disulfonated poly(arylene ether sulfone) plasticized with poly(ethylene glycol) for membrane formation

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ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form
30 January 2014
Accepted 3 February 2014
Available online 11 February 2014

Keywords:
Sulfonated polysulfone
Poly(ethylene glycol)
Bueche-Harding master curve

ABSTRACT

Disulfonated poly(arylene ether sulfone) (BPS) random copolymers, prepared from a sulfonated monomer, have been considered for use as membrane materials for various applications in water purification and power generation. These membranes can be melt-processed to avoid the use of hazardous solvent-based processes with the aid of a plasticizer, a low molecular weight poly(ethylene glycol) (PEG). PEG was used to modify the glass transition temperature and melt rheology of BPS to enable coextrusion with polypropylene (PP). Our previous paper discussed the miscibility of BPS with PEG and the influence of PEG on the glass transition of BPS. In this study, the rheological properties of disulfonated poly(arylene ether sulfone)s plasticized with poly(ethylene glycol) (PEG) are investigated to identify coextrusion processing conditions with candidate PPs. The effects of various factors including PEG molecular weight, PEG concentration, temperature and BPS molecular weight on blend viscosity were studied. The rheological data effectively lie on the same master curve developed by Bueche and Harding for non-associating polymers such as poly(methyl methacrylate) (PMMA) and polystyrene (PS). Although sulfonated polysulfone contains ionic groups, the form of its viscosity versus shear rate (or frequency) behavior appears to be dominated by the relaxation of polymer entanglements.

1. Introduction

Most ion containing membranes used for desalination [1–3] and electrodialysis [4,5], etc. are prepared using solvent-based processing methods. For example, polyamide (PA) thin film composite membranes, the state-of-art membrane in reverse osmosis, are produced by interfacial polymerization at a water/solvent interface [1,2]. Solution processing has several disadvantages including environmental and health hazards and the high costs associated with solvent disposal. As a result, better methods of preparing membranes are of some interest.

Sulfonated polysulfone is a potential alternative membrane material for water purification [6–10] and fuel cell applications [5,11–15], owing to its good ion transport properties as well as good thermal and mechanical stability [5–15]. Moreover, unlike most membranes, which can only be produced by solution processing, sulfonated polysulfone membranes may be prepared via a solvent-free extrusion using rather benign plasticizers; e.g., poly(ethylene glycol) [16]. This plasticizer enables the extrusion processing of sulfonated polysulfone and can be removed from the extruded membrane by water extraction. In addition, composite membranes may be obtained by coextrusion with a proper support material that can be made porous by stretching or by laminating the sulfonated polysulfone layer onto a porous support layer [17–19]. The objective of this study is to investigate the formation of sulfonated polysulfone desalination membranes without the use of solvents.

Bebin et al. have reported on a similar approach for extruding post-sulfonated polysulfone films for proton exchange membrane fuel cell (PEMFC) materials. Proton conductivity and life span of the extruded films were compared with those of solvent cast films [20,21]. Sanchez et al. also used post-sulfonated polysulfone for PEMFC. The influence of several plasticizers on the glass transition and rheological properties of the post-sulfonated polysulfone was reported [22–26]. These previous studies have focused on fuel cell applications, and the possibility of membrane

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http://dx.doi.org/10.1016/j.polymer.2014.02.011
0032-3861/

Table 1
Characteristics of the polymers of this study.

Material	$\overline{M}_w$[a] [g/mol]	IV[a] [ml/g]	T_g[b,e] [°C]	Density[c,e] [g/cm^3]	Water Permeability[d] [L μm m^{-2} h^{-1} bar^{-1}]	NaCl rejection[d] [%]
BPS-20K	33,900	48.2	273	1.30	0.03	99.2
BPS-20K	45,500	61.8	273	1.31	0.03	99.2
BPS-20K	56,700	72.3	273	1.35	0.03	99.2

[a] Determined by SEC using NMP with 0.05 M LiBr at 50 °C. Note that specific refractive index increment (dn/dc) values were measured using an assumption of 100% mass recovery. dn/dc values for BPS-20K polymers of this study are 0.17 [ml/g].
[b] Measured by DSC at 20 °C/min.
[c] Measured using a Mettler Toledo density determination kit (Part# 238490, Switzerland) with *n*-heptane (Cat# 32287, Sigma–Aldrich, St. Louis, MO) at ambient temperature (20–22 °C).
[d] Table 1 from Ref. [10].
[e] Measurements were conducted using solution cast films. Transparent and uniform thickness films (30∼40 μm) were formed by the solution casting method reported previously [16].

formation for water purification applications has not been explored.

Thin film composite membranes are composed of an active selective layer supported by a porous layer. The active layer provides high water transport and salt rejection while the porous layer provides a mechanical support with minimal obstruction of water flow [2,27]. This study examines the feasibility of composite membranes that might be useful for desalination prepared via coextrusion of a sulfonated polysulfone with a suitable support layer material [17]. Polypropylene (PP) is considered as a candidate support material for the proposed membranes since porous PP can be readily formed by a number of approaches involving post-extrusion stretching [18,19].

In this study, disulfonated poly(arylene ether sulfone)s (BPS) blended with PEG plasticizers have been explored to identify appropriate extrusion formulations for membrane applications. Previously, we reported the effect of various PEG materials on the blend glass transition temperature and the thermal stability of these PEGs at potential melt processing temperatures [16]. This paper reports rheological properties of the plasticized sulfonated polysulfone to identify formulations that are rheologically compatible for coextrusion with PP. The effects of various factors including PEG molecular weight, concentration, temperature and BPS molecular weight on the complex viscosity of blends are investigated. An approach by Bueche and Harding was employed to generalize the rheological behavior of the blends and to compare it with that of non-associating polymers [28,29]. A subsequent paper will report on the transport properties and morphology of the extruded sulfonated polysulfone membranes relative to solution cast films.

2. Experimental

2.1. Materials

The disulfonated poly(arylene ether sulfone) random copolymers (BPS-XY) used in this study were synthesized by direct aromatic nucleophilic substitution step polymerization, as established by McGrath et al. (See Fig. 1) [6,8–10,30]. The nomenclature for these polymers is BPS-XY, where *X* is the mole percent (mol%) of sulfone groups in the polymer (i.e., disulfonated monomer), and Y is the cation, such as H (acid form) or K (potassium form). For instance, BPS-20K consists of 20 mol% of disulfonated monomer in the potassium form.

BPS polymers prepared in the K form were supplied by Akron Polymer Systems (Akron, OH) and were used as received. In this study, the potassium form of the sulfonated polysulfone, or BPS-K form was chosen due to its good thermal stability [9,16]. To explore the effect of plasticizers on the melt behavior of sulfonated polysulfone, BPS-20K (ion exchange capacity (IEC) = 0.92 meq/g) was used because of its good membrane performance as well as chemical and thermal stability at extrusion conditions [6,8,10,16]. Polymers with various molecular weights ($\overline{M}_w$ = 33,900–56,700 g/mol) were used to investigate the effect of molecular weight on viscosity. Selected properties are summarized in Table 1.

Note that the polydispersity (PDI) of sulfonated polysulfone from step growth polymerization is around 2 [31], although the ratio of $\overline{M}_w/\overline{M}_n$ determined by Size Exclusion Chromatography (SEC) is around 1.4∼1.5. This is related to the characteristics of light scattering measurements employed for SEC, which have a tendency to overestimate number average molecular weight ($\overline{M}_n$) since the light scattering measurements are not sensitive to the lower molecular weight portion of the molecular weight distribution, as reported previously [32]. The molar mass determined by the light scattering measurements is the weight average molecular weight ($\overline{M}_w$) and therefore we report $\overline{M}_w$s of BPS-20K materials as shown in Table 1.

2.2. Plasticizer

Poly(ethylene glycol), PEG, materials were used as plasticizers in this study, and their physical properties are summarized in Table 2 [16]. These PEGs were purchased from Sigma Aldrich (St. Louis, MO) and were used as received. Product details are PEG 200 Cat# P3015, PEG 300 Cat# 202371, PEG 400 Cat# 202398, and PEG 600 Cat# 87333.

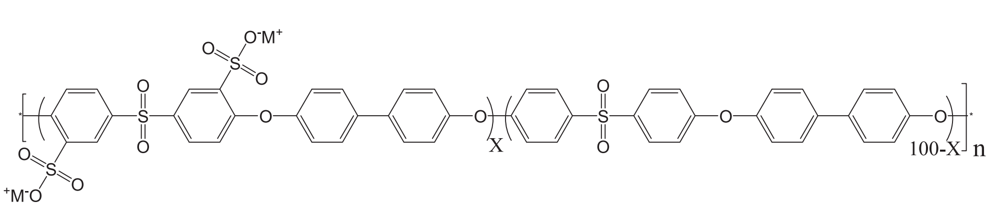

Fig. 1. Chemical structure of disulfonated poly(arylene ether sulfone) random copolymer: for BPS-XY series, *X* = mol% of disulfonated monomer (0 < *X* < 100), Y = H (acid form) or K (potassium salt form).