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Ionomer thermodynamic interrelationships associated with wettability, surface energy, swelling, and water transport

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ABSTRACT

Polytetrafluoroethylene (PTFE), perfluorosulfonic acid (PFSA), sulfonated poly(phenylene) (sPP), and (poly[t-butyl styrene-b-hydrogenated isoprene-b-sulfonated styrene-b-hydrogenated isoprene-b-t-butyl styrene) (tBS-HI-S-HI-tBS or PBC) films wetting properties and surface energy were evaluated by measuring their contact angles. Increasing ionomer sulfonate group concentration led to an equivalent decrease in contact angle due to increasing surface energy. Owens and Wendt, Wu, and Kwok and Neumann's models were used to estimate these material's total surface energy (γ_S); and their dispersive (γ_S^d) and polar (γ_S^p) force components. The Owens and Wendt model provided reasonable γ_S, γ_S^d, and γ_S^p estimates for sPP with an ion-exchange capacity (IEC) of 1.8 that had a predicted γ_S of 25.4 mJ/m^2, and a PBC series with an IEC ranging from 0.0 to 2.0 having a γ_S change from 14.1 to 23.5 mJ/m^2 due to increasing sulfonic acid group concentration. PFSA's γ_S was best fit using the Kwok and Neumann model (γ_S = 19.1 mJ/m^2). Ionomer film swelling behavior in water was evaluated at steady-state, and as a function of time. These results revealed anisotropic swelling in all dimensions (x, y, and z) with the greatest change in the film's thickness and the smallest in its manufacturing processing direction. In general, film swelling was characterized as Fickian with the exception being Nafion 212 (NF212) that was non-Fickian. Steady-state changes in film mass due to water swelling were used to estimate effective diffusion coefficients D_w. However, highly processed Nafion 212 had non-Fickian diffusion properties. Material γ_S, swelling behavior, and water transport characteristics were dependent upon chemical composition and IEC.

1. Introduction

Surface wettability is difficult to measure when compared to liquid surface tension [1]. Several approaches have been used to estimate a solid surface tension; including direct force [2], contact angle [3], capillary penetration into a particle filled column [4], particle sedimentation [5], particle solidification front interactions [6], film flotation [7], gradient theory [8], Lifshitz theory of van der Waals' forces [9], and the theory of molecular interactions [10]. Stamm calculated polymer surface energy (γ_s) using liquid contact angle experiments [11]. Shimizu used Neumann's, Fowkes'; and geometric and the harmonic mean correlations that were combined with Young's relationship in order to calculate the γs of polypropylene, polystyrene, and a liquid crystalline polymer by measuring their contact angles using various liquids at 20 °C [12]. Gennes developed theory describing a contact angle, wetting transition, and the dynamics of spreading [13]. Geoghegan reviewed polymer

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blends boundary-layers and the growth of wetting areas, polymer film dewetting, and pattern formation caused by chemically organized substrates during dewetting [14].

There are several factors impacting polymer wettability and swelling. Fasolka and Mayes emphasized the role of film thickness and surface energetics up the morphology and surface chemistry of compositionally symmetric diblock copolymers. This effort revealed that surface composition and topography affected γ_s, which impacted lithographic masks and photonic materials at multiple length scales [15]. Andruzzi evaluated chemical structure effects upon wetting surfaces using 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO), fluorinated polystyrene, and polystyrene-block-polyisoprene block copolymers [16]. Tsibouklis created films with molecular designed features that produced ultra-low surface energy characteristics [17]. Wang showed that a patterned poly(dimethylsiloxane) (PDMS) stamp was capable of modifying the wettability of two ionomers using poly(3,4-ethylenedi-oxythiophene)-poly(styrenesulfonate) (PEDOT-PSS), and polyelectrolyte poly(sodium 4-styrenesulfonate) (NaPSS) [18]. Kanakasabai studied the relationships between ion-exchange capacity (IEC), proton conductivity, water sorption, predicted surface energy, and wettability characteristics using blends of polyvinyl alcohol (PVA) and sulfonated poly(ether ether ketone) (SPEEK) [19]. During polymer wetting, swelling occurs that has generated numerous experiments, simulations, and models attempting to predict its properties [20]. Solute adsorption and diffusion into a polymer is characterized by a balanced interaction between network and solvent molecules, which can significantly modify its properties [21]. During solvent transport through a film; free volume changes occur, plasticization, and solvent coupling that increases molecule diffusivity through a film [21b]. In this paper, basic relationships between surface energy, wetting, and water transport are considered with respect to ionomer composition and structure.

2. Experimental

2.1. Materials

Polytetrafluoroethylene (PTFE) Flat-Form dishes were used as received from VWR International, LLC. Polyphenylene (PP) was prepared using a Diels-Alder reaction, and sulfonated to generate sulfonated poly(phenylene) (sPP). The overall synthetic process for PP and sPP is described elsewhere [22]. A series of perfluorosulfonic acid (PFSA) ionomers used in this study were Nafion films created by DuPont. The films evaluated were NF115, NF117, and NF212 purchased from Ion Power, Inc. PBC ionomers were provided by Kraton Polymers LLC, Houston, TX [23]. These ionomers are poly[t-butyl styrene-b-hydrogenated isoprene-b-sulfonated styrene-b-hydrogenated isoprene-b-t-butyl styrene) that is also referred to as PBC or tBS-HI-S-HI-tBS [23a]. The material's structure and basic characteristics are shown in Fig. 1 and summarized in Table 1.

Absolute anhydrous 200 proof ethyl alcohol ACS/USP grade was used as received from PharmcoAaper. Ethylene glycol or EG (99 + %) was obtained from Geel Belgium. Pre-cleaned 75 × 50 mm micro-slides were purchased from Sigma-Aldrich. All films were attached to micro-slides using Scotch Permanent Double-Sided Tape in order to create uniformly flat surfaces.

2.2. Experimental methods

2.2.1. Membrane preparation

PBC solutions with an IEC equal to 1.0, 1.5, and 2.0 were supplied in a 1:1 wt% cyclohexane:heptane solution (C/H). After evaporating the original solvent, the precipitated solid was dissolved in THF, $CHCl_3$, and C/H, which was recast into films by

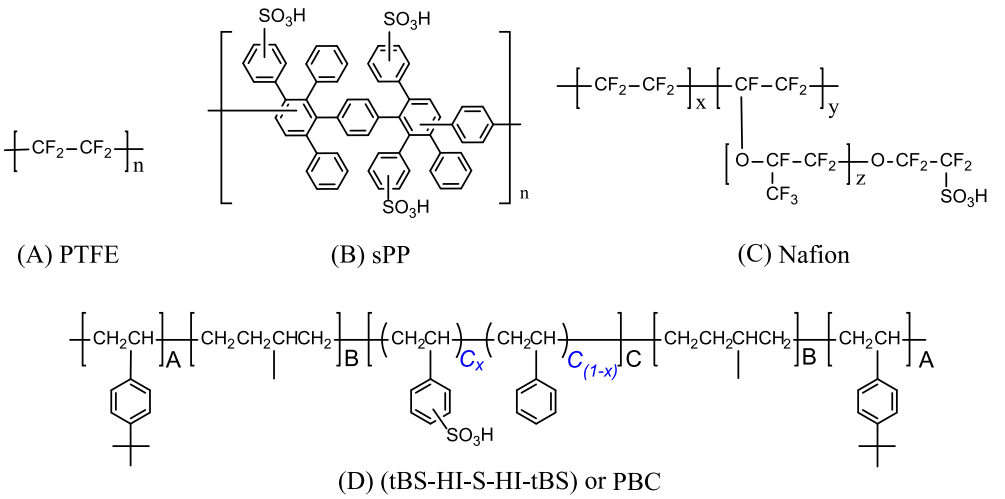

Fig. 1. Polymer structures for (A) PTFE, (B) sPP, (C) Nafion, and (D) PBC.