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Semi-interpenetrating Polymer Networks of Poly(4-styrenesulfonic acid) and Poly(acrylic acid) for Fuel Cell Applications

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Abstract

Semi-interpenetrating networks (sIPN) of poly(4-styrenesulfonic acid) and crosslinked poly(acrylic acid) were prepared to use as proton-conducting membranes in fuel cells. The effects of molar ratio of PSSA to PAA and degree of crosslinking on membrane properties, including hydrophilicity, water stability, and thermal stability, were studied. The membrane with low PSSA content and maximum degree of crosslinking exhibited the lowest hydrophilic and highest water resistant properties. Thermogravimetric analysis (TGA) indicated that the membranes were stable up to approximately 200 °C under nitrogen atmosphere. Scanning electron microscopy (SEM) observation suggested the homogeneity of sIPN membrane.

Keywords: fuel cell, interpenetrating networks, polyelectrolytes

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have received a lot of attention as power sources for vehicles and electronic devices due to their high efficiency and environmental friendly properties (1-2). A good polymer electrolyte membrane should have high proton conductivity, low electron conductivity, low permeability to fuel, good oxidative and hydrolytic stabilities, and good mechanical properties. The current polyelectrolyte membranes (PEMs) used, are generally based on hydrated sulfonated polymers. Among these, Nafion®, a perfluorosulfonic acid membrane introduced by Dupont, has drawn much interest because of its chemical and electrochemical stabilities. However, the high cost of perfluoroether comonomers and the safety concerns of tetrafluoroethylene in the synthesis are the major drawbacks.

Poly(4-styrenesulfonic acid) (PSSA) has been considered as a promising choice for PEM because of its low cost and relative high proton conductivity. A composite material of PSSA and phosphotungstic acid

(PWA) prepared by solvent-casting method showed an extremely high proton conductivity of 1 x 10^{-2} S/cm at 180 ºC under dry nitrogen flow (3). This observation could be attributed to the fast proton transfer occurred at the interface of PWA-encapsulated structure.

Interpenetrating polymer networks (IPNs) are a subset of polymer blends, and can be obtained by several methods including mixing linear prepolymers and their respective crosslinking agent following by curing the blend. Although these networks exhibit no covalent bond, they are held together by permanent chain entanglement, leading to higher levels of molecular mixing than for simple molecular mixtures. Semi-interpenetrating polymer networks (sIPN) differ from IPN in that they are composed of one linear polymer entrapped within the networks of another polymer. In a study of sIPN membranes of sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK) and poly(acrylic acid) (PAA), the membranes showed high proton conductivity and good dimensional stability, which was due to permanent entanglements of the cross-linked PAA and SPPESK (4). High mechanical stability, good water retention capacity, and low methanol permeability were observed in poly(vinyl alcohol) and PSSA sIPN (5).

In this work, semi-interpenetrating networks of PSSA and PAA using ethylene glycol as a crosslinker of AA were prepared. PSSA was used as a proton source, and crosslinked networks of PAA were used to improve the mechanical property of the membrane. The effects of molar ratio of PSSA to PAA and degree of crosslinking on membrane properties, including hydrophilicity, water and thermal stabilities, were investigated. Surface morphology of the membrane was characterized using SEM.

2. Materials and Methods

2.1 Materials

Poly(4-styrenesulfonic acid) (PSSA, MW ~75,000, 18 wt.% in water) and poly(acrylic acid) (PAA, MW 100,000, 35 wt.% in water) were purchased from Aldrich. Ethylene glycol (EG, reagent grade) was purchased from Carlo Erba. All chemicals were used as received.

2.2 Characterization

Fourier Transform Infrared (FTIR) spectra were measured on a PerkinElmer FTIR spectrometer (spectrumOne) measuring in the range of 4000–500 cm^{-1} with 16 scans. Contact angles were measured with an FTA 1000 Drop Shape Instrument, B Frame with FTA Video Drop Shape Software. Water stability test was conducted by immersing 1 cm x 1 cm membranes in 10 mL of deionized (DI) water at room temperature. Thermogravimetric analysis (TGA) was carried out using SDT 2960 (TA instruments) with a heating rate of 10 °C/min from 30 to 600 °C under nitrogen. Samples were coated with gold before a surface study by SEM (LEO 1450VP, UK).

2.3 Membrane preparation

Desired amounts of PAA aqueous

solution (35 wt.%) and ethylene glycol were added into PSSA aqueous solution (18 wt.%). The solutions were stirred for 10 min prior to casting on Teflon plate, and drying at 80 °C in an oven for 4 h. The membranes were peeled off, and then heated at 120 °C in an oven for 2 h to induce crosslinking reaction.

3. Results and Discussion

3.1 Membrane compositions

PSSA-PAA network membranes, shown in Fig. 1, were successfully prepared and the chemical structures were confirmed using FTIR spectroscopy. The obtained membranes were designated as xPSSA-yPAA-zEG, where x, y, and z are molar equivalences of PSSA, PAA, and EG, respectively. The four samples were listed as 0.5PSSA-1PAA-0.5EG, 0.25PSSA-1PAA-0.5EG, 0.25PSSA-1PAA-0.25EG, and 0.25PSSA-1PAA-0.1EG, with crosslinking degrees of 100, 100, 50, and 20, respectively.

FTIR spectra of PSSA-PAA membranes were shown in Fig. 2. Peaks corresponding to PSSA at 1159, 1031, 830 and 772 cm^{-1} were observed. The peaks at 1159 and 1031 cm^{-1} were assigned to S=O asymmetric and symmetric stretches (6). The wagging vibrations of C-H in 1,4- and 1,2-substituted benzene rings of PSSA were shown at 830 and 772 cm^{-1}, respectively (7). The peaks at 3430, 1720, and 1450 cm^{-1} corresponded to PAA. As expected, the intensity of the hydroxyl peak at 3430 cm^{-1} increased with decreasing amount of the crosslinker. An appearance of a new peak at 1623 cm^{-1} in the sample with lowest degree of crosslinking suggested a formation of hydrogen bonds (8).

3.2 Hydrophilicity and water stability

Since polymers containing sulfonic acid groups transport protons via vehicular mechanism, relying on the presence of water, the hydrophilicity of the membranes were evaluated using water contact angle measurement. Water was dropped onto the sample surface, and the images were captured immediately. Refer to Table 1, when PSSA content was increased, the contact angle decreased due to the

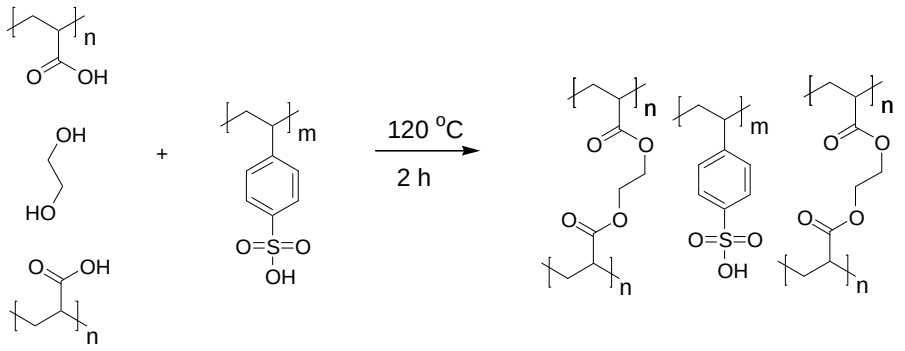

Figure 1. Synthetic scheme of PSSA-PAA interpenetrating networks in conjunction with ethylene glycol.

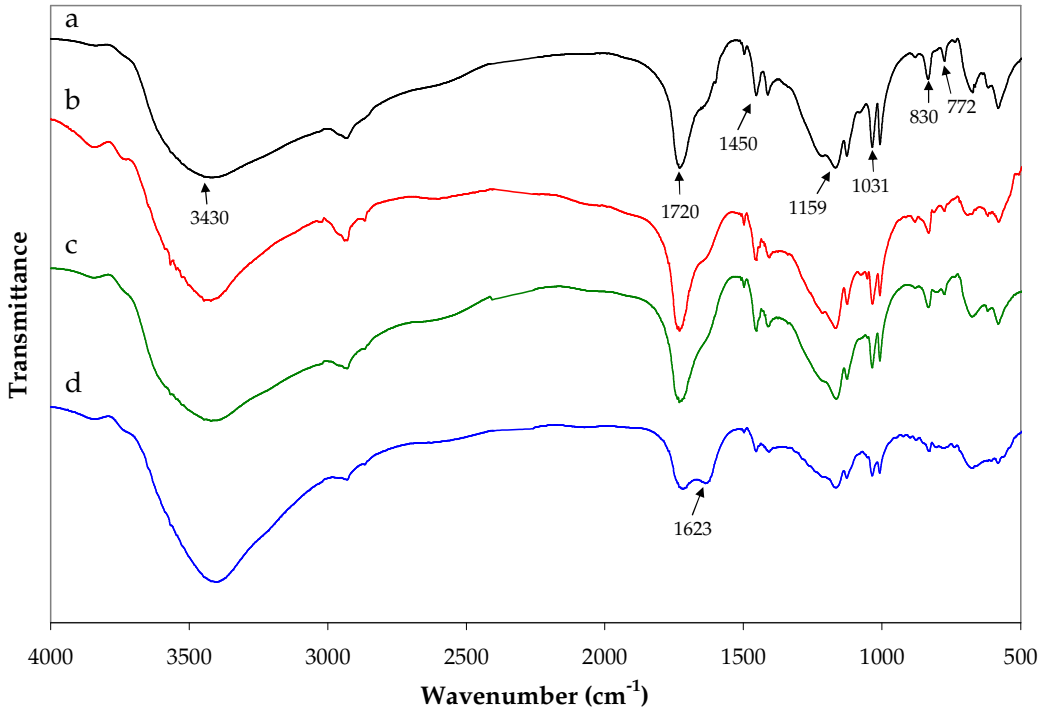

Figure 2. FTIR spectra of PSSA-PAA sIPN membranes: (a) 0.5PSSA-1PAA-0.5EG; (b) 0.25PSSA-1PAA-0.5EG; (c) 0.25PSSA-1PAA-0.25EG; (d) 0.25PSSA-1PAA-0.1EG.

Table 1. Water contact angles on PSSA-PAA interpenetrating network membranes.

Samples	Water contact angle (°)
0.5PSSA-1PAA-0.5EG	61
0.25PSSA-1PAA-0.5EG	77
0.25PSSA-1PAA-0.25EG	64
0.25PSSA-1PAA-0.1EG	60

hydrophilicity of PSSA. Smaller contact angles were observed with lower degrees of crosslinking. This could be attributed to numerous carboxyl groups of acrylic acid present after the crosslinking (4), and a looser polymer network which allowed water to penetrate through more easily.

The stability of the membranes against water was studied by immersing the membranes in DI water at room temperature. The 0.25PSSA-1PAA-0.5EG membrane was the most hydrolytically stable, and no physical change was observed for at least 24 h of immersion in water. This result agrees well with the least hydrophilic nature of the sample suggested from the

contact angle study.

3.3 Thermal stability

Thermogravimetric analysis results were shown in Fig. 3. All membranes were thermally stable up to 200 °C. TGA thermograms showed three main degradation stages. The first weight loss below 200 °C was attributed to the loss of absorbed water. The second weight loss between 200 and 340 °C was likely due to the loss of polymeric side chains. The decomposition of polymeric main chains was observed in the temperature range of 340-480 °C (9-10). By lowering the crosslinking degree, the decomposition rate slightly increased. Comparing the membranes with the same degree of crosslinking, the membrane with higher PSSA content showed a larger weight loss in the first decomposition stage, and this was due to the hygroscopic nature of PSSA.

3.4 Membrane miscibility

Microphase separation in a PEM is undesirable since it leads to fuel crossover and resistance to proton transfer. The miscibility of the IPNs can be verified by the absence of phase separation observed by SEM or transmission electron microscopy (TEM) (11). Refer to SEM image of 0.5PSSA-1PAA-0.5EG membrane in Fig. 4, no phase separation was observed.

4. Conclusions

Semi-interpenetrating networks of PSSA and crosslinked PAA were successfully prepared and confirmed by FTIR spectroscopy. The hydrophobicity and

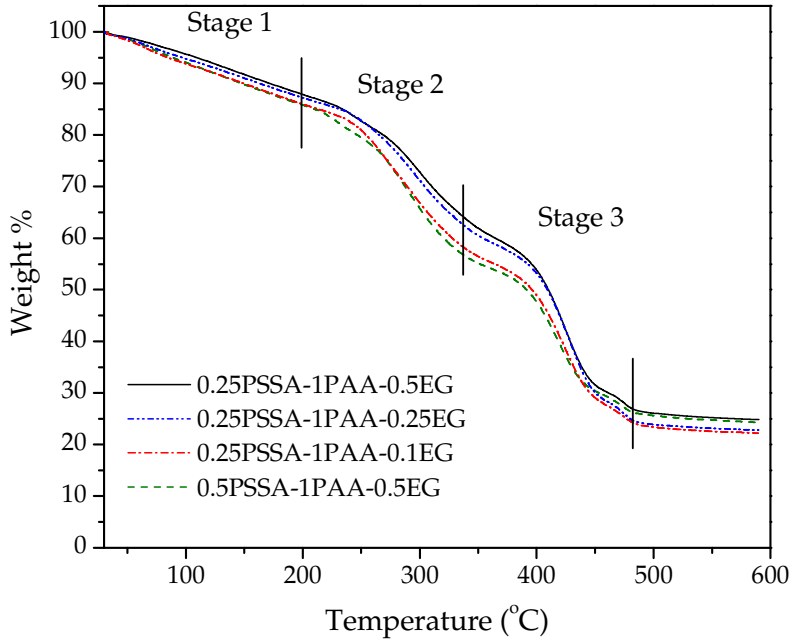

Figure 3. TGA thermograms of PSSA-PAA membranes.

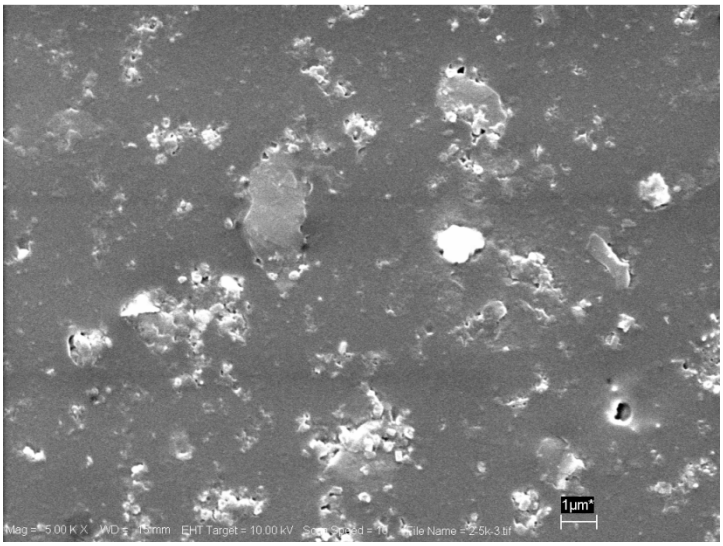

Figure 4. SEM image of 0.5PSSA-1PAA-0.5EG membrane (5k magnification).

water resistant property increased with decreasing PSSA to PAA molar ratio and increasing crosslinking degree. Moreover, all membranes showed similar thermal stability. PSSA content and crosslinking degree did not significantly affect the thermal decomposition. SEM micrograph suggested that sIPN membrane was homogenous.

5. Acknowledgement

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