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Radiolytic preparation and characterization of hydrophilic poly (acrylonitrile-*co*-vinylsulfonate)-grafted porous poly (tetrafluoroethylene) substrates

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HIGHLIGHTS

- The hydrophobic surface of a porous PTFE substrate was modified to the hydrophilic surface.
- A mixture of AN and SVS was co-grafted into the PTFE film by γ-ray irradiation.
- The hydrophilic substrate is used for the impregnation of polymer electrolyte.

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ABSTRACT

In this study, a hydrophilic copolymer of acrylonitrile (AN) and sodium vinylsulfonate (SVS) was grafted into a highly hydrophobic porous poly(tetrafluoroethylene) (PTFE) substrate using a gamma-ray irradiation method and the grafted substrate was used as a substrate for impregnating a hydrophilic ionomer, Nafion. The results of FT-IR and TGA analysis of the prepared substrate showed that the SVS/AN monomers were successfully grafted into the porous PTFE film. The results of degree of grafting, elemental analyzer, and contact angle analysis showed that the hydrophilicity of the prepared PTFE-*g*-P(AN-*co*-VS) substrate was increased with an increase in the amount of SVS/AN graft copolymers. Also, the results of FE-SEM and Gurley number measurement showed that the pores in the substrate were reduced as the amount of SVS/AN copolymers grafted into the substrate increased. The prepared porous PTFE-*g*-P (AN-*co*-VS) substrate at an irradiation dose of 70 kGy was found to impregnate Nafion ionomer effectively compared to the original porous PTFE substrate. These results suggest that the prepared PTFE-*g*-P (AN-*co*-VS) substrate can be effectively used for the impregnation of polymer electrolyte (Nafion) to prepare a reinforced composite membrane.

1. Introduction

Recently, reinforced composite membranes using a porous substrate have attracted attention as a polymer electrolyte membrane for fuel cell application owing to several advantages including fabrication of a thin membrane, lower cost, and excellent thermal and mechanical properties (Hirokazu et al., 2005; Teruaki et al., 2005; Nguyen and Wang, 2010; Kim et al., 2004). The most common substrate used in the preparation of the reinforced composite membranes is a porous PTFE film (Ramya et al., 2006; Liu et al., 2003) with chemical resistance, high thermal stability, and excellent mechanical properties (Ahn et al., 2004; Zhu et al., 2008; Lin et al., 2004; Tang et al., 2007a, 2007b). However, the preparation of the reinforced composite membrane using porous PTFE substrate has major difficulties of how to impregnate the hydrophilic a polymer electrolyte well into the hydrophobic porous PTFE substrate and how to introduce good interfacial compatibility between polymer electrolyte and PTFE (Lin et al., 2004; Tang et al., 2007a, 2007b; Zhu et al., 2007). To overcome these problems, it is necessary that the hydrophobic surface of the porous PTFE substrate be converted into a hydrophilic surface.

It was reported that the hydrophobic surface of a PTFE polymer can be modified into a hydrophilic surface by chemical treatment, plasma treatment, and radiation (Kang and Zhang, 2000). Chemical treatment has been shown to introduce various hydrophilic functional groups into a PTFE film, but it has difficulty in

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monitoring and controlling the depth profile of the introduced functional group on the surface (Kang and Zhang, 2000). Surface modification by plasma treatment is simple, reliable, and cost-effective. However, some drawbacks of the technique include the aging effect of the plasma-treated surfaces in air, the lack of molecular design capability, and the lack of spatial distribution of the functional groups on the substrate surface (Kang and Zhang, 2000; Chan and Ko, 1996; Chatelier et al., 1995). Irradiation treatment using various irradiation sources including UV (Katan et al., 1998), an electron beam (Lappan et al., 1999; Burger et al., 1993), ion beam (Svorcik et al., 1998; Zhang et al., 2000), and γ-ray (Jun and Qunji, 1998; Akihiro et al., 1999) have been exploited for the surface modification of a porous PTFE substrate. These techniques generate radicals onto a porous PTFE substrate followed by introducing a hydrophilic polymer chain through graft polymerization using hydrophilic monomer. In these techniques, various hydrophilic polymers can be easily introduced onto a porous PTFE substrate and the hydrophilicity can be easily controlled by adjusting the irradiation dose and grafting conditions (Kang and Zhang, 2000).

The commercially available hydrophilic monomers containing the carboxylic group (–COOH) and sulfonic acid group (–SO_3H) including maleic anhydride (MA), acrylic acid (AA), sodium allylsulfonate (SAS), sodium styrene sulfonate (SSS), vinyl acetate (VAc), and glycidyl methacrylate (GMA) have been utilized in the radiation grafting (Sohn et al., 2013; Izumi and Ranby, 1973; Choi and Nho, 2000; Misra et al., 1987). In particular, the monomers with a sulfonic acid group are very useful to introduce the hydrophilicity due to its high ionic character (Behar et al., 1982).

Recently, we reported that SAS and acrylonitrile (AN) monomers can be grafted into a porous PTFE substrate using a radiation grafting method (Park et al., 2014). It was found that the radiation grafting of SAS monomer alone is difficult to be achieved due to mainly the lower reactivity toward a radical polymerization. Therefore, an AN monomer having a high reactivity was mixed with a SAS monomer, and the monomer mixture was used for the radiation grafting to introduce a hydrophilic SAS/AN copolymer into the porous PTFE substrate.

In this study, a mixture of an AN monomer and sodium vinylsulfonate (SVS) monomer, which is the simplest monomer containing a sulfonic acid group, was applied for the introduction of a hydrophilic copolymer into a hydrophobic porous PTFE substrate using a simultaneous irradiation method. Various analysis techniques using FT-IR, TGA, an elemental analyzer, a contact angle analyzer, FE-SEM, and a densometer were performed to characterize the prepared PTFE substrates, and their results are reported in this paper.

2. Experimental

2.1. Materials

Sumitomo Electronic's Poreflon (30 μm thickness), a porous polytetrafluoroethylene (PTFE) was used as a substrate for the radiation grafting. Grafting monomers, sodium vinylsulfonate (SVS, 25% in water, 2.3 mol/L) and acrylonitrile (AN, 99.0%) were purchased from Tokyo Chemical Industry and Showa Chemical Company, respectively. A Nafion solution (Dufont™, Nafion® D2021, 20 wt% in isopropanol and water) was used as a polymer electrolyte to be impregnated into the grafted substrate. As a grafting solvent, methanol (Showa Chemical Company, 99.8%) was used. All other reagents used in this experiment did not go through an additional refining process.

2.2. Radiation grafting process

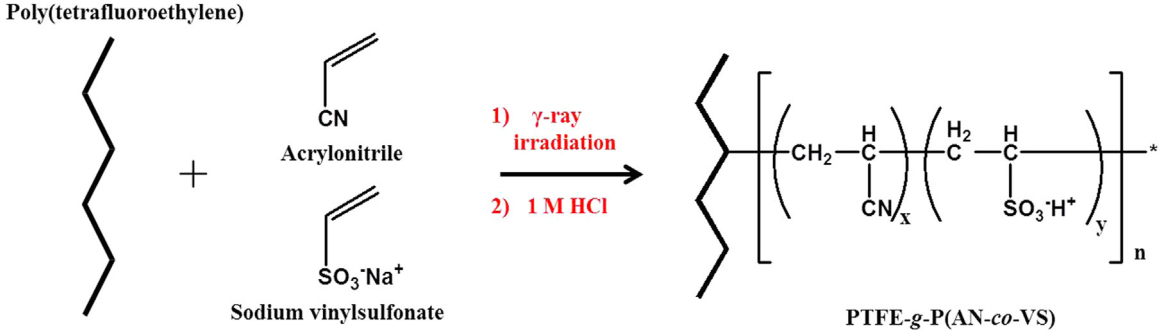
PTFE substrates were washed with methanol and dried in a 50 °C vacuum oven for 12 h prior to radiation grafting. For the preparation of the grafting solution, SVS monomer (2.3 M) in water and AN monomer (2.3 M) in methanol were mixed at a 1:1 mole ratio. The porous PTFE substrate was added into a vial containing the prepared SVS/AN monomer solution and the nitrogen was then bubbled into the vial for 10 min to remove oxygen from the solution. The grafting solutions containing porous PTFE substrates were irradiated using Co^{60} γ-rays at irradiation dose ranges of 20–240 kGy with a dose rate of 10 kGy/h at room temperature (Scheme 1).

The substrates were washed with *N*,*N*-dimethylformamide (DMF) three times to remove the homopolymers and dried in a 60 °C vacuum oven for 12 h. The dried substrate was soaked in a 1 M HCl solution to substitute all Na^+ ions of SVS with H^+ ions for 24 h. The prepared substrate was then washed with distilled water numerous times and dried in a 60 °C vacuum oven for over 12 h to obtain a porous PTFE-*g*-P(AN-*co*-VS) substrate with a sulfonic acid group (–SO_3H). The degree of grafting of the grafted porous substrate was calculated from formula (1) below. Here, W_o indicates the weight of the dried porous PTFE substrate before grafting, and W_g indicates the weight of the grafted PTFE-*g*-P(AN-*co*-VS) substrate after grafting.

$$DOG(\%) = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

2.3. Preparation of Nafion-impregnated composite membrane

The impregnation of Nafion was performed using a dip-coating method. The solvent of a commercial Nafion solution consists of water and isopropanol. During the drying process of the Nafion-coated porous PTFE substrate at high temperature, the coated layer was found to be easily cracked because the solvent was evaporated



Scheme 1. Radiation grafting procedure of AN and SVS repeat units in the copolymer onto PTFE substrate.