



Poly(vinylbenzyl sulfonic acid)-grafted poly(ether ether ketone) membranes



Mi-Lim Hwang, Jisun Choi, Hyun-Su Woo, Vinod Kumar, Joon-Yong Sohn, Junhwa Shin*

Research Division for Industry and Environment, Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, 29 Geomgu-gil, Jeongeup-si, Jeollabuk-do 580-185, Republic of Korea

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ABSTRACT

In this study, an aromatic hydrocarbon based polymer electrolyte membrane, poly(vinylbenzyl sulfonic acid)-grafted poly(ether ether ketone) (PEEK-g-PVBSA), has been prepared by the simultaneous irradiation grafting of vinylbenzyl chloride (VBC) monomer onto a PEEK film and subsequent sulfonation. Each chemical conversion was monitored by FT-IR and SEM-EDX instruments. The physicochemical properties including IEC, water uptake, proton conductivity, and methanol permeability of the prepared membranes were also investigated and found that the values of these properties increase with the increase of degree of grafting. It was observed that the IEC values of the prepared PEEK-g-PVBSA membranes with 32%, 58%, and 80% DOG values were 0.50, 1.05, and 1.22 meq/g while the water uptakes were 14%, 20%, and 21%, respectively. The proton conductivities (0.0272–0.0721 S/cm at 70 °C) were found to be somewhat lower than Nafion 212 (0.126 S/cm at 70 °C) at a relative humidity of 90%. However, the prepared membranes showed a considerably lower methanol permeability ($0.61\text{--}1.92 \times 10^{-7} \text{ cm}^2/\text{s}$) compared to a Nafion 212 membrane ($5.37 \times 10^{-7} \text{ cm}^2/\text{s}$).

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1. Introduction

The excessive use of fossil fuels has become a serious global issue since it causes exhaustion of fossil fuels and environmental problems such as global warming and pollution. Therefore, many efforts have been made to find an efficient and effective energy source that can substitute fossil fuels in the future, and hydrogen has been considered as a very promising candidate. A fuel cell using hydrogen as a fuel is very attractive since it not only avoids the emission of greenhouse gases and other air pollutants, but also shows a high energy conversion efficiency [1]. It has been continuously considered as the main power source for automobiles, portable devices, power back-up, and auxiliary power units.

In a polymer electrolyte membrane (PEM) fuel cell and direct methanol fuel cell, PEM plays a key role in determining the performance of the fuel cells by acting as a conductor of protons as well as a physical barrier between the fuel and oxidant [2]. Currently, Nafion, a fluorocarbon polymer membrane, has been widely used in these fuel cells because of its good chemical and mechanical properties as well as high proton conductivity. Nevertheless, it has some disadvantages such as high cost, fuel crossover, and de-

creased proton conductivity at high temperature [3–5]. Thus, it is necessary to develop a low-cost and efficient membrane having excellent properties for fuel cell applications.

Recently, aromatic hydrocarbon polymers such as poly(ether ether ketone) (PEEK), polyimide (PI), polybenzimidazole (PBI), polyphenylene (PP), poly(ether sulfone) (PES), and polyphosphazene have been gaining a lot of attention as a backbone of PEM owing to their excellent chemical resistance and thermal stability, low cost, low methanol permeability, and high durability [6–13]. Among the aromatic hydrocarbon polymers, PEEK is a very attractive polymer because of its excellent chemical properties along with abrasion, high temperature, hydrolysis, flame, and gamma ray resistant abilities. To incorporate a sulfonic acid group as a proton conducting group into a PEEK polymer backbone, both (1) post sulfonation of commercial PEEK polymer with sulfuric acid, and (2) co-condensation with sulfonated monomer have been extensively studied [14–17].

The radiation-induced graft polymerization is known to be a useful method to prepare polymer electrolyte membranes (PEM) for fuel cells [18,19]. The most frequently used grafting monomer for the preparation of fuel cell membrane is styrene, which is readily available, cheap, and prone to sulfonation at the aromatic ring of the polystyrene graft chain to give poly(styrene sulfonic acid) (PSSA) as an ion conducting polymer, and meanwhile, fluorocarbon polymer films such as polytetrafluoro-

* Corresponding author. Tel.: +82 63 570 3575; fax: +82 63 570 3089.

E-mail address: shinj@kaeri.re.kr (J. Shin).

ethylene (PTFE), polytetrafluoroethylene-co-hexafluoropropylene (FEP), poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA), poly(ethylene-*alt*-tetrafluoroethylene) (ETFE), and poly(vinylidene fluoride) (PVDF) films are mainly used as a grafting backbone film owing to their excellent chemical and mechanical properties [20–26].

In the previous work [27–28], styrene was used to introduce PSSA graft chains onto a PEEK film by a radiation grafting method followed by treatment with chlorosulfonic acid for sulfonation. However, the prepared membranes suffered from some serious problems like a higher value of water uptake (over 200%) owing to the sulfonation on the PEEK backbone as well as on the graft chains. It has been observed that a higher and randomized degree of sulfonation affects the water uptake ability as well as the ion exchange capacity (IEC), which further affect the performance of the membranes. To overcome these problems, ethyl 4-styrenesulfonate was used as a grafting monomer to avoid the sulfonation to PEEK backbone polymer [29,30]. The results obtained from these findings were proved to be very useful regarding the preparation of aromatic hydrocarbon polymer based fuel cell membranes with improved properties such as high proton conductivity and excellent durability. The high durability made available the thin PEEK film as a membrane backbone. It was also found that the PEEK membrane based fuel cell has stable and excellent performance at high temperature [31,32]. However, one disadvantage of this process is that ethyl 4-styrene sulfonate grafting monomer is not readily available from a commercial supplier. It was also suggested that it is difficult to confirm the exact structure of the grafted membrane especially at the linked position of styrene on PEEK film, and that graft polymerization is initiated by the phenoxy radicals generated by the scission of ether linkages under the influence of radiation, which further results in block type grafts instead of conventional T-shape grafts like in the grafting of styrene onto polyethylene (PE), polypropylene (PP), or PTFE.

Recently, we also developed a novel synthetic approach using vinylbenzyl chloride (VBC) as a grafting monomer to introduce poly(vinylbenzyl sulfonic acid) graft chains onto fluoropolymer backbone films such as FEP, PFA, and ETFE [33–35]. It has been found that the prepared membranes not only showed considerably lower methanol permeability, but also exhibited higher proton conductivity as compared to Nafion. It was also observed that they have higher chemical stability compared to the membranes with poly(styrene sulfonic acid) graft chains. VBC has two reactive functional groups, a chloromethyl and a vinyl group that make it more advantageous than other monomers since the chloromethyl group can be easily converted into various functional groups (i.e. quaternary amines, phosphoric acid, and sulfonic acid etc.) after graft polymerization. For the synthesis of poly(vinylbenzyl sulfonic acid)-grafted membranes, the chloromethyl group of poly(vinylbenzyl chloride) graft chain has been converted into a sulfonic acid group by the subsequent treatments with thiourea, sodium hydroxide, and finally hydrogen peroxide. In this process, selective sulfonation to the aliphatic chloromethyl group can be achieved without affecting the phenyl rings of the graft chains. This result naturally led us to apply this mild sulfonation process for the preparation of PEEK based membranes with sulfonated graft chains.

In our previous work, we demonstrated that VBC monomer can be grafted onto a PEEK film through a simultaneous irradiation method [36]. In this study, poly(vinylbenzyl chloride)-grafted PEEK films were subjected for the preparation of PEEK based membranes with poly(vinylbenzyl sulfonic acid) graft chains, and the resulting membranes were further applied to explore the potential for fuel cell application.

2. Experimental

2.1. Materials

PEEK film with 50 μm thickness was supplied by Victrex and washed with ethanol to remove any impurities. VBC (mixture of *m*- and *p*-isomers, 96%) and thiourea were purchased from Sigma–Aldrich Co. Ltd. and used as received. Solvents such as dichloromethane (DCM), ethanol, *N*-methyl pyrrolidone (NMP), 30 wt.% hydrogen peroxide aqueous solution, sodium hydroxide, and acetic acid were purchased from commercial suppliers and used without further purification.

2.2. Radiation grafting

50 μm PEEK films (5×20 cm) were immersed in the mixture of vinylbenzyl chloride and dichloromethane. The mixtures were purged with nitrogen and then subjected to a simultaneous irradiation using a gamma-ray from a ^{60}Co source at a dose rate of 2 kGy/h. The detailed grafting condition for PVBC-grafted film with 32%, 58%, and 80% DOG (degree of grafting) are shown in Table 1. After irradiation, the grafted films were washed with toluene and dried in a vacuum oven. The degree of grafting was calculated using the following Eq. (1): W_o is the original sample weight and W_g is the grafted sample weight.

$$\text{DOG} = [(W_g - W_o) / W_o] \times 100 \quad (1)$$

2.3. Sulfonation

The prepared PEEK-g-PVBC films were immersed in a 1.3 M thiourea in a NMP solution at 70 $^{\circ}\text{C}$ for 15 h to convert the chloride moiety to the thiouronium salt. The reacted films with the thiouronium salt moiety were washed with distilled water and then treated with a 3 M sodium hydroxide in a methanol solution (distilled water:methanol = 1:3 vol. ratio) at 40 $^{\circ}\text{C}$ for 12 h for hydrolysis. The resulting film was washed with distilled water and then immersed in a mixture of a 30 wt.% hydrogen peroxide aqueous solution and acetic acid (30:70 vol. ratio) at room temperature for overnight. The prepared membrane was washed several times with distilled water and dried at 60 $^{\circ}\text{C}$ in a vacuum oven.

2.4. Instrumental analysis

The preparation process of the membrane was monitored by the FT-IR spectrometer (Tensor-37, Bruker) under ambient conditions in transmittance mode at 4000–600 cm^{-1} . The thermal properties of the samples were characterized by thermogravimetric analysis (TGA) (SDT Q600, TA Instrument Co. Ltd.). About 10 mg samples were heated from 40 to 650 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ under a dry nitrogen atmosphere.

SEM-EDX (Scanning Electron Microscopy–Energy Dispersive X-ray spectroscopy, 7200-H, Horiba Co. Ltd.) measurement was conducted to investigate the cross-section distribution pattern of the functional group over the PEEK films. The membrane was cut and fixed on carbon tape of the SEM holder. The cross-section of

Table 1
Radiation grafting condition of PEEK-g-PVBSA.

	VBC conc. (Vol.%)	Dose rate (kGy/h)	Total dose (kGy)	DOG (%)
DOG32	50	2	40	32
DOG58	60	2	40	58
DOG80	65	2	30	80

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