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Polymer electrolyte membranes prepared by EB-crosslinking of sulfonated poly(ether ether ketone) with 1,4-butanediol

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ABSTRACT: Crosslinked sulfonated poly(ether ether ketone) (SPEEK) membranes were prepared through the electron beam (EB)-irradiation crosslinking of SPEEK/1,4-butanediol under various irradiation conditions and used as a proton exchange membrane (PEM) for fuel cell applications. The crosslinked membranes were characterized by gel fraction, a universal testing machine (UTM), dynamic mechanical analysis (DMA), and small-angle X-ray scattering (SAXS). The gel fraction of the crosslinked membranes was used to estimate the degree of crosslinking, and the gel fraction was found to be increased with an increase of the crosslinker content and EB-absorbed dose. The UTM results indicate that a brittle EB-crosslinked membrane becomes more flexible with an increase in the crosslinker content. The DMA results show that the EB-crosslinked membranes have well-developed ionic aggregation regions and the cluster T_g of membranes decrease with an increase in the 1,4-butanediol crosslinker content. The SAXS results show that the Bragg and persistence distance of crosslinked membranes increase with an increase in the crosslinker content. The proton conductivities of the EB-crosslinked membranes were more than 9×10^{-2} S/cm. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41760.

KEYWORDS: crosslinking; irradiation; membranes

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INTRODUCTION

Ion-exchange membranes are widely applied for various industrial applications, such as electro-dialysis,[1] batteries,[2] chlor-alkali cell,[3] artificial muscles,[4] and fuel cells.[5–8] The most used commercial ion-exchange membrane is Nafion (Dupont), which is composed of a polytetrafluoroethylene (PTFE) segment and perfluoroether side chains terminated with sulfonic acid groups. It has various advantages such as excellent chemical stability, mechanical properties, and high proton conductivity.[8] However, the membrane also has many disadvantages, for example, high production costs, high methanol crossover, and decreased proton conductivity at temperatures above 80°C.[6,9–13] Therefore, as an alternative to Nafion, many research groups have focused on aromatic hydrocarbon based ion-exchange membranes, such as sulfonated polyimide,[14] sulfonated polyphosphazene,[15,16] sulfonated poly(arylene ether),[17,18] and sulfonated poly(ether ether ketone),[19–21] which have high-temperature stability, low methanol permeability, environmental compatibility, and low cost. In particular, sulfonated poly(ether ether ketone) (SPEEK) has been considered a good candidate because it has excellent thermal, chemical, and mechanical properties and the proton conductivity can be easily controlled by the sulfonation conditions, such as the reaction time, temperature, and sulfonic acid content. However, the SPEEK membrane with a high degree of sulfonation is well known to be hampered by particularly low mechanical properties and dimensional stability owing to the excessive water swelling.[22–24] Therefore, many research efforts to prepare more stable and mechanically strong membranes have also been undertaken through several methods, such as the addition of hydrophilic inorganic materials, blending with polymeric materials, and the formation of a crosslinking network.[25–29]

Crosslinking is thought to be a simple and powerful method to improve the low mechanical properties and dimensional stability. Recently, Mao *et al.*[30] reported that crosslinked SPEEK membranes with aromatic or aliphatic amines have improved mechanical properties and dimensional stability. Mikhailenko *et al.*[31] reported that SPEEK membranes with a crosslinked structure were prepared using a thermal crosslinking method under a vacuum for 48–72 h at 130–150°C using di-or triols (ethylene glycol and glycerol). The crosslinked membrane also showed increased mechanical properties and reduced water swelling with an increase in the degree of crosslinking, although some of the available sulfonic acid groups for the proton transfer are sacrificed for the crosslinking reaction with alcohol. Gupta and Choudhary[32] also reported crosslinked SPEEK membranes with poly(ethylene glycol) by a thermal crosslinking method under a vacuum at 60°C (2 h), 80°C (2 h), 100°C (2 h), 120°C (2 h), and 135°C (16 h). The crosslinked membrane was found to have not only improved mechanical properties but also increased proton conductivity under low relative humidity condition. Zhao *et al.* utilized poly (vinyl alcohol) as a crosslinker for the crosslinking of sulfonated poly(arylene ether ketone) (SPAEK) containing pendent carboxyl groups using a thermal crosslinking method. Compared to a Nafion membrane, it was observed that the proton conductivity of the prepared membrane was higher, while the methanol permeabilities were lower.[33] On the other hand, Zhong *et al.*[34] developed a novel crosslinked SPEEK membrane by introducing UV-crosslinkable vinyl groups followed by UV-irradiation. The water uptake of the crosslinked membrane was reduced from 29.3 to 26.1% and the tensile strength was increased from 40.3 to 63.4 MPa. The proton conductivity of the crosslinked membrane was slightly decreased with an increase in the irradiation time.

Among the various crosslinking methods available, an electron beam (EB)-irradiation method has been widely used for polymeric material processing in the various industrial fields, such as crosslinked radial tires, coating, heat shrinkable tubing, and heat-resistance wires and cables because of its inherent advantages over the thermal crosslinking and UV-irradiation method.[35] The advantages include high reactivity, a fast processing time, no need for an initiator or catalyst, a deep penetration ability, and resistance to the oxygen inhibitor in the surface area. These advantageous characteristics can save the processing time and energy of production. In addition, the product can be ready to use immediately after the irradiation. Since the EB has high penetration ability, uniform crosslinking can be achieved at both the surface and inner part of the product. In our previous study, a crosslinked SPEEK membrane was prepared by the EB-irradiation crosslinking of a mixture of SPEEK and crosslinkers including polyester acrylate, trimethylolpropane triacrylate, 1,6-hexandiol diacrylate, and 2-(2-ethoxy-ethoxy)ethyl acrylate. It was found that by increasing the absorbed doses, the mechanical properties, thermal stability, and water uptake of the crosslinked SPEEK were significantly improved.[36,37]

In this study, we demonstrate that 1.4-butanediol can be used as a crosslinker in the preparation of crosslinked SPEEK membranes using an EB-irradiation method. Several EB-crosslinked SPEEK membranes were prepared by irradiating a mixture of SPEEK and 1,4-butanediol under various irradiation conditions, such as absorbed doses, and 1,4-butanediol content. Among the many candidate multi-hydroxyl alcohols, 1,4-butanediol was selected as a crosslinker since it was thought to have a sufficient chain length with flexibility that can avoid the brittleness of the resulting crosslinked membranes. The EB-crosslinked SPEEK membrane were characterized using a thermogravimetric analysis (TGA), universal testing machine (UTM), dynamic mechanical analysis (DMA), and small-angle X-ray scattering (SAXS). The water uptake, ion exchange capacity, and proton conductivity were also investigated to estimate the possible usage for the fuel cell membranes.

EXPERIMENTAL

Materials

The poly(ether ether ketone) powder was supplied by Victrex company (UK). Sulfonic acid and *N*,*N*-dimethyl acetamide (DMAc) were supplied by the Showa chemical industry Co. (Japan). 1,4-butanediol was purchased from the Sigma-Aldrich Co. (St. Louis, MO, USA). Other chemical reagents were used as received without further purification.

Sulfonation of PEEK

PEEK was dried in a vacuum at 130°C for at least 12 h prior to sulfonation. PEEK powder (21 g) was slowly added to sulfuric acid (98 wt %, 500 mL) at room temperature under a N_2 atmosphere. After the PEEK dissolved completely, the solution was stirred at 60°C for 3 h. The polymer solution was then cooled to 5°C in an ice water bath to terminate the reaction and poured into a large amount (ca. 5 times volume) of ice-saturated water to give a fibrous type SPEEK polymer. The resulting polymer was washed with deionized water until the pH of the washing solution became neutral. The polymer was dried at room temperature for 2 days and then at 130°C for overnight in a vacuum oven. The sulfonation degree (SD) was determined from the ratio between the peak area of the protons near the sulfonic acid group and the integrated peak area of the peaks equivalent to all the other aromatic protons in the ^{1}H-NMR spectra, according to Zaidi *et al.*'s work.[19] The SD of the prepared membrane was calculated as 67% from the ^{1}H-NMR data.

Preparation of EB-Crosslinked membranes

To prepare the casting solution, the SPEEK powder and 1,4-butanediol were dissolved in DMAc to form a 10 wt % solution (the weight ratio of SPEEK powder to 1,4-butanediol was set to 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, and 40/60) and the solutions then cast onto glass plates. The cast solutions were dried in an oven at 70°C for 40 min until the solution reached a gel state, and were then irradiated by electron beams from the electron beam linear accelerator at Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute (Jeongup, Korea) at irradiation doses ranging from 50 to 400 kGy with a dose rate of 6 kGy/min at room temperature. The residual solvent of the irradiated membranes was removed at 80°C for 4 h in a convection oven, and in a vacuum oven at 100°C for 1 day. The membranes were separated from the glass plate by immersion in deionized water for several minutes. The membranes were immersed in an aqueous 1 *M* HCl solution for 2 days, and then in deionized water for 1 h. The membranes were dried in a vacuum oven at 120°C for 1 day.

Gel Fraction

The gel fraction was estimated from the weight change of the irradiated SPEEK membrane after immersing the membrane in DMAc. The prepared samples were placed in a 200 mesh stainless steel bag and then immersed in a DMAc solvent for 12 h at room temperature. The immersed samples were dried in a vacuum oven at 100°C for 24 h prior to the weight measurement of the remaining samples. The gel fraction[38] value was calculated using the following equation:

$$\text{Gel fraction (\%)} = W_{\text{after dissolved}} / W_{\text{dry}} 100 \tag{1}$$

where W_{dry} is the weight of the dried membrane, and $W_{\text{after dissolved}}$ is the weight of the remaining membrane after dissolution.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) analysis of the unirradiated/irradiated SPEEK membranes and the unirradiated/irradiated SPEEK/1,4-butanediol membranes was performed using an Varian 640 spectrometer (Varian, Australia). The FT-IR spectra were obtained in ATR mode in the range of 600–4000 cm^{-1} at a resolution of 2 cm^{-1}.

Thermogravimetric Analysis

The thermal stability of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes was determined using an SDTQ600 (TA Instruments, Newcastle, DE, USA). The membranes were heated up to 160°C under an air atmosphere, and maintained this temperature for 5 min to remove the moisture completely. The sample was cooled down to 40°C and then reheated up to 800°C with a heating rate 10°C/min.

Tensile Strength Analysis

The mechanical property of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes was measured using stress-strain static tests with an INSTRON series IX (Instron Co., (Norwood, MA, USA) UTM System model 4400). The crosslinked SPEEK membranes were cut into a rectangular form (5.3 mm × 50 mm). The distance between two grips was fixed at 31 mm, and the UTM test speed was set to 50 mm/min at room temperature. To reduce experimental errors, more than five samples were prepared and applied for the measurement of the tensile strength data.

Ion Exchange Capacity and Water Uptake

The ion exchange capacity (IEC) of unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes was measured using a titration method. Vacuum-dried membranes were first immerged into an aqueous 1 *N* NaCl solution for 24 h to exchange H$^+$ with Na$^+$. The solution was subsequently back-titrated with a 0.1 *N* NaOH solution using an automatic titrator DL22 (Mettler Toledo Company, Switzerland). The IEC value was calculated using the following equation:

$$\mathrm{IEC} = [C_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}}] \;/\; W_{\mathrm{dry}} \tag{2}$$

where C_{NaOH} is the concentration of the NaOH solution, V_{NaOH} is the volume of the 0.1 *N* NaOH aqueous solution consumed for the volumetric titration, and W_{dry} is the weight of the dry unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes. For determination of the water uptake, all of the samples were dried in a vacuum oven at 120°C for 1 day before the measurements. The samples were then immersed and maintained in de-ionized water for 3 h at 30 and 75°C to attain equilibrium water uptake. The water uptake value was calculated using the following equation:

$$\text{Water uptake (\%)} = (W_s - W_{\mathrm{dry}})/W_{\mathrm{dry}}100 \tag{3}$$

where W_s and W_{dry} are the weights of swollen and dried samples, respectively.

Dynamic Mechanical Analysis

A DMA experiment of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes was performed on a TA DMA Q800 (TA Instruments). The crosslinked SPEEK membranes were dried at 120°C under a vacuum for 12 h prior to the thermal mechanical analysis. The dried films with a width of 5.3 mm were carried out in a tensile mode at 1 Hz from −100°C to 300°C with a heating ramp of 2°C/min under a N_2 atmosphere.

Small-Angle X-ray Scattering

The SAXS experiment was conducted at Station 4C of the Pohang Accelerator Laboratory II (PAL II) synchrotron radiation source (Pohang, Korea). The unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes were completely neutralized to contain Na$^+$ counter ions by soaking the H$^+$-form films in an excess aqueous NaCl solution. The neutralized membranes were washed to remove excess NaCl and then dried in a vacuum oven at 110°C for 12 h. The incident X-ray beam was tuned to a wavelength of 0.675 Å, and the sample-to-detector distance was set to 1059 mm. The size of the beam at the sample was smaller than 1 mm^2. The two-dimensional scattering patterns were recorded on a high-resolution Mar CCD camera with a 15 second exposure time. The SAXS data were plotted as the relative intensity versus the scattering vector (q) after correction for the sample absorption and background. q is a function of the scattering angle (θ), as shown in the following relationship:

$$q = \frac{4\pi}{\lambda}\sin(\theta) \tag{4}$$

where λ is the wavelength of radiation and θ is half of the scattering angle (2θ).

Proton Conductivity

The proton conductivity of unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes in H$^+$-form was measured using an AC impedance analyzer (SI 1260, Solatron Company) with a four-point probe method. The proton conductivity of crosslinked SPEEK membranes was determined at 90% relative humidity (RH) after treatment with a 1 *M* HCl solution. All membranes were washed and hydrated with deionized water prior to the measurements. The impedance measurements were recorded in the frequency region from 0.01 to 100 kHz. The proton conductivity (σ, S/cm) was calculated as follows:

$$\sigma = L/(AR) \tag{5}$$

where L is the distance between the two probes (cm), A is the cross-sectional area of the membrane (cm^2), and R is the electrical resistance (Ω).

RESULTS AND DISCUSSION

The effects of various crosslinking conditions, such as absorbed dose and 1,4-butanediol content on the degree of crosslinking of the crosslinked membranes were investigated by a gel fraction.[38,39] The gel fraction is an indirect method of measuring the degree of crosslinking of the crosslinked membranes. Figure 1 shows the relationship between the gel fraction measured at various EB-absorbed doses and the 1,4-butanediol crosslinker contents included in the SPEEK solution prior to the crosslinking process. It was observed that the gel fraction of the EB-crosslinked membranes was gradually increased with an increase of the crosslinker content and EB-absorbed dose, indicating that

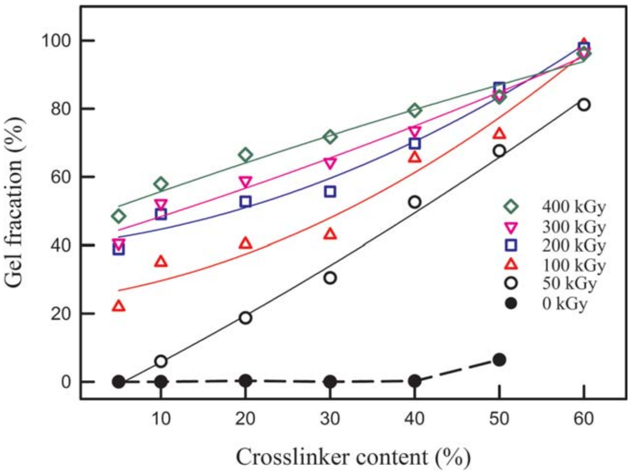

Figure 1. Gel fraction of unirradiated/irradiated SPEEK/1,4-butanediol membranes as a function of the absorbed dose and 1,4-butanediol crosslinker content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

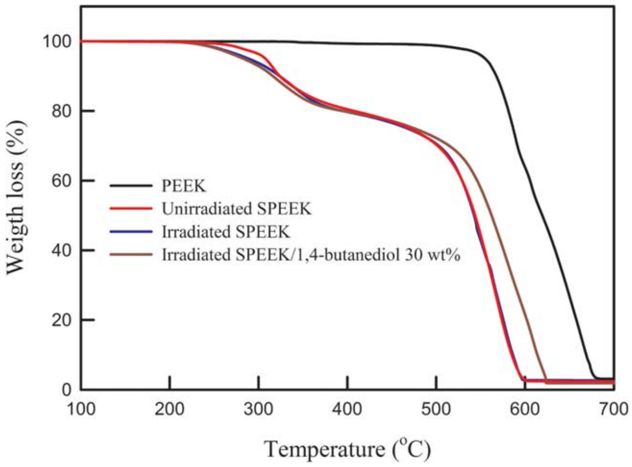

Figure 3. TGA curves of PEEK, unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the degree of crosslinking of the EB-crosslinked membrane was largely affected by the crosslinker content and EB-absorbed dose. To exam the thermal crosslinking effect of SPEEK/1,4-butanediol under dry conditions (at 80°C for 4 h in a convection oven and in a vacuum oven at 100°C for 1 day) used in this study, SPEEK/1,4-butanediol membranes with various crosslinker content (5–50 wt %) were thermally treated under dry conditions without EB-irradiation. It was observed that the gel fraction values of the membranes with 1,4-butanediol content from 5 to 40 wt %, cannot be obtained since they are completely dissolved after 12 h soaking in DMAc, while the gel fraction value of the membrane with 50 wt % of 1,4-butanediol content was measured to be only 6%. These results indicate that the crosslinking of EB-irradiated SPEEK/1,4-butanediol membranes proceeds mainly through EB-irradiation rather than through thermal treatment. In this study, the SPEEK membranes prepared by the irradiation of 300 kGy in the presence of various contents of 1,4-butanediol (10–40%) were used for the characterization of the membranes.

The FT-IR spectra of the unirradiated/irradiated SPEEK membranes and unirradiated/irradiated SPEEK/1,4-butanediol (30 wt %) membranes were obtained using an FT-IR spectrometer operated in ATR mode (Figure 2). The broad characteristic absorption peak at 3400 cm^{-1} can be attributed to the stretching vibration of the O—H group from the sulfonic acid group and the associated water molecules.[31] The stretching vibration peak of the carbonyl group was also found at 1654 cm^{-1}. IR peaks at 1597, 1497, 1473, and 1408 cm^{-1} can be assigned to the stretching vibration peaks of the aromatic C=C from the SPEEK backbone chain.[40] Asymmetric and symmetric stretching vibration peaks of O=S=O from the sulfonic acid group

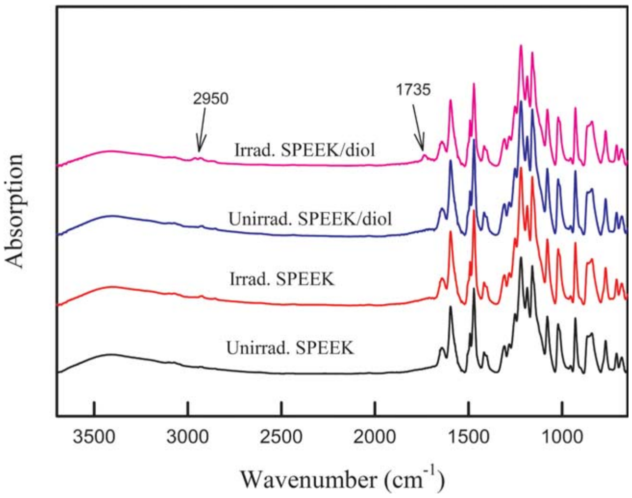

Figure 2. FT-IR spectra of the unirradiated/irradiated SPEEK membranes and the unirradiated/irradiated SPEEK/1,4-butanediol membranes. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

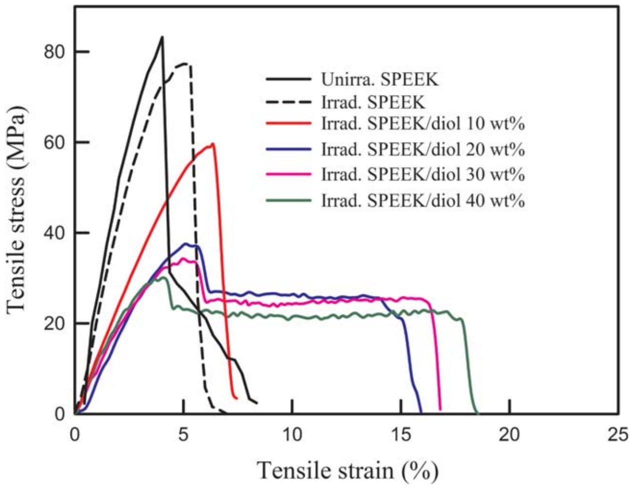

Figure 4. Mechanical tensile stress versus strain plots of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Mechanical Property Data of the SPEEK, Unirradiated/Irradiated SPEEK, and Irradiated SPEEK/1,4-Butanediol Membranes

Sample name	Young's modulus (*E*)	Yield point (MPa)	Stress at break (MPa)	Elongation at break (%)
Unirrad. SPEEK	23.6	82.3	82.3	8.18
Irrad. SPEEK	15.3	76.7	76.7	5.33
Irrad. SPEEK/diol 10 wt %	11.7	59.0	59.0	6.42
Irrad. SPEEK/diol 20 wt %	10.1	37.7	25.8	14.1
Irrad. SPEEK/diol 30 wt %	9.7	34.2	25.4	16.2
Irrad. SPEEK/diol 40 wt %	9.6	29.7	22.6	17.9

appeared at 1250 and 1080 cm^{-1}. In addition, the IR peaks at 1020 and 705 cm^{-1} were yielded due to the S=O stretching and S−O stretching,[40] respectively. It was found that the FT-IR spectrum of unirradiated SPEEK/1,4-butanediol membrane was very similar to that of the unirradiated SPEEK membranes. This result implies that the 1,4-butanediol crosslinker was mostly removed during the washing process, and no significant structural changes occurred during the drying condition. For the irradiated SPEEK/1,4-butanediol membrane, a new peak was observed at 1735 cm^{-1}, which is considered due to the stretching vibration peak of the carbonyl groups from ester, acid or aldehyde.[31] Another IR peak observed at 2950 cm^{-1} can be assigned to C−H stretching vibration from the alkane group of 1,4-butanediol. The presence of the aliphatic C–H peak indicates that the 1,4-butanediol crosslinker remained in the irradiated SPEEK/1.4-butanediol membrane despite the washing process with water since 1,4-butanediol was attached to the SPEEK chain during the EB-irradiation process. At this moment, the crosslinking mechanism between SPEEK and the 1,4-butanediol crosslinker is somewhat unclear since the FT-IR spectra did not provide sufficient evidence for the mechanism. By considering the inertness of the PEEK backbone chain against EB-irradiation reported by Al Lafi,[41] the crosslinking is considered to proceed through the coupling of the sulfonic acid of SPEEK and the hydroxyl group of 1,4-butanediol.

The thermal stability and degradation behavior of pure PEEK, unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol (30 wt %) membrane were determined by TGA under an air atmosphere (Figure 3). In the results, pure PEEK exhibits a one degradation step from 550 to 680°C, which can be attributed to the thermal degradation of the PEEK main chain. For the unirradiated and irradiated SPEEK membranes, two different degradation steps were observed in the temperature ranges of 250–380 and 510–600°C, respectively. The first step can be attributed to the decomposition of the sulfonic acid group, while the second step can be attributed to the thermal degradation of the PEEK main chains.[42] In the case of the irradiated SPEEK/1,4-butanediol membrane, two different degradation steps were also observed in temperature ranges of 250–380 and 520–620°C. However, the second degradation temperature ranges were shifted to a high temperature region, indicating that the thermal stability of the irradiated SPEEK/1,4-butanediol membrane was increased by the formation of the crosslinked structure.

To estimate the mechanical properties of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes, the stress versus strain curves were measured using a UTM. Figure 4 shows the stress versus strain curves of the unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol membranes. The values of Young's modulus, yield point,

Table II. The Value of Theoretical IEC, Experimental IEC, and Water Uptake of the Unirradiated/Irradiated SPEEK, and Irradiated SPEEK/1,4-Butanediol Membranes

Membranes	Theoretical IEC (meq/g)	Experimental IEC (meq/g)	Water uptake (%)	
			30°C	70°C
Unirrad. SPEEK	1.92	1.89	44.2	Unable
Irrad. SPEEK	1.92	1.88	43.8	Unable
Irrad. SPEEK/diol 5 wt %	1.82	1.76	47.5	385.8
Irrad. SPEEK/diol 10 wt %	1.70	1.76	38.0	333.3
Irrad. SPEEK/diol 20 wt %	1.51	1.72	35.4	305.8
Irrad. SPEEK/diol 30 wt %	1.32	1.67	33.3	220.8
Irrad. SPEEK/diol 40 wt %	1.13	1.66	25.9	164.5
Irrad. SPEEK/diol 50 wt %	0.95	1.63	25.9	119.7
Irrad. SPEEK/diol 60 wt %	0.76	1.61	17.5	104.6

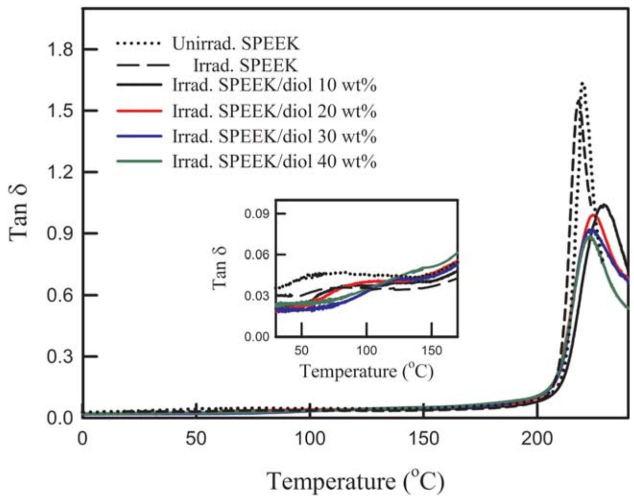

Figure 5. Loss tangent of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes as a function of temperature, measured at 1 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stress at break, and elongation at break are summarized in Table I. It was found that the Young's modulus, yield point, and stress at break of the irradiated SPEEK membrane were slightly decreased compared to the unirradiated SPEEK membrane. These results indicate that some structural changes such as chain scissoring may occur during the EB-irradiation process. In addition, the values of Young's modulus, yield point, and the stress at break were significantly decreased with an increase in the crosslinker content while the elongation at the break was increased. These results indicate that the brittle EB-crosslinked membrane become more flexible with an increase in the crosslinker content. Generally, the mechanical properties, such as Young's modulus, yield point, stress at break, and elongation at the break depends upon five factors, namely, the chain interaction, chain mobility, chain stiffness, chain length, and free volume.[43] For example, with increases in the amount of aliphatic crosslinker and the length of the aliphatic crosslinker chain, it is known that the free volume of the polymer increases and the chain interaction decreases. The increased free volume and the decreased chain interaction are also known to increase the flexibility. Therefore, the increased flexibility of the irradiated SPEEK/1,4-butanediol membranes is considered to be due to the aliphatic crosslinker added in the EB-crosslinked membrane.

It is well-known that the ionic exchange capacity (IEC), defined herein as the amount sulfonic acid groups per gram of membrane largely affects the water uptake and proton conductivity of the membrane. The IEC values of the unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol membrane were measured using an acid-base titration method and the results are listed in Table II. It was found that the unirradiated SPEEK and irradiated SPEEK have similar IEC values, indicating that the sulfonic acid group of SPEEK was not significantly affected by the EB-absorbed dose. In addition, the IEC value of irradiated SPEEK/1,4-butanediol membranes was decreased from 1.76 to 1.61 meq/g with an increase in the 1,4-butanediol crosslinker content. This is mainly due to the increased weight percent of uncharged crosslinker in the crosslinked membranes. It was also shown that the IEC values of the crosslinked membranes were measured to be higher than the theoretical IEC values, especially when a larger amount of 1,4-butanediol crosslinker mixture was added into the casting solution. The observed higher IEC values of the crosslinked membranes is considered due to the loss of unreacted 1,4-butanediol crosslinker from the membranes during the washing process with water. The water uptake of the membrane is known to have a crucial effect on the proton conductivity and mechanical properties because a proton can be transported along with the cluster network channel (i.e., hydrated ionic aggregation) of a proton exchange membrane.[44] Therefore, the proton exchange membrane needs enough water uptake for a proton to be easily transported through the cluster network channel. However, an excessive water uptake in the membrane causes a decrease of the mechanical property and dimensional stability. Thus, it is important to measure the water uptake of the crosslinked membranes. Table II also shows the water uptake of the EB-crosslinked membranes and thermally crosslinked membranes measured at a temperature range of 30–70°C. The value of the water uptake of all crosslinked membranes was decreased with an increase in the crosslinker content owing to the increase of crosslinked network that limits the polymer chain mobility.

The thermal and mechanical properties of the crosslinked membranes were determined using the DMA technique. The loss tangent curves for unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol membranes can be seen in Figure 5. In the results, the unirradiated SPEEK, the irradiated SPEEK, and all of the irradiated SPEEK/1,4-butanediol membranes showed two different loss tangent peaks. According to the EHM (Eisenberg-Hird-Moore) model for amorphous

Table III. The Glass Transition Temperature and Ionic Modulus of the Unirradiated/Irradiated SPEEK and Irradiated SPEEK/1,4-Butanediol Membranes

Sample name	Matrix T_g (°C)	Cluster T_g (°C)	Ionic modulus (MPa)
Unirrad. SPEEK	69.2	219.6	2640
Irrad. SPEEK	69.6	218.2	2544
Irrad. SPEEK/diol 10 wt %	101.2	228.2	2772
Irrad. SPEEK/diol 20 wt %	115.8	225.6	2893
Irrad. SPEEK/diol 30 wt %	145.5	223.8	2916
Irrad. SPEEK/diol 40 wt %	155.7	222.6	3038

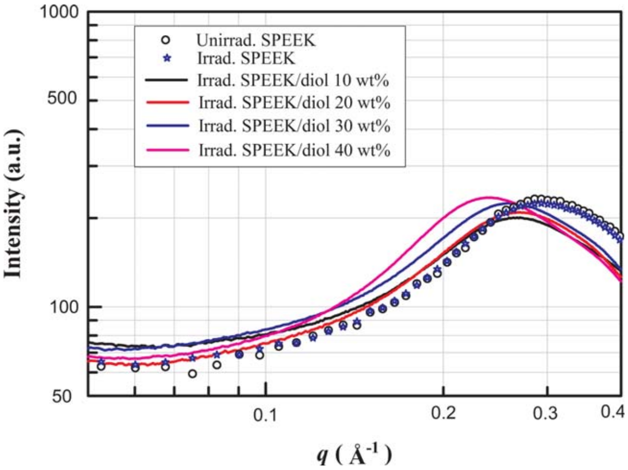

Figure 6. Small angle X-ray scattering profile of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes as a function of the 1,4-butanediol crosslinker content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

random ionomers, the ionic aggregates, called multiplets, lead to a decrease in the mobility of the polymer chains surrounding them.[45–47] When the concentration of the ionic group increases, the regions of the polymer chain with restricted mobility start to overlap and become large and continuous regions called clusters. At this point, the amorphous random ionomer starts to exhibit two glass transition temperatures (T_g's); the T_g at low temperature is due to the matrix glass transition temperature (i.e., matrix T_g), while the T_g at high temperature is due to the cluster glass transition temperature (i.e., cluster T_g). The values of matrix T_g and cluster T_g of all membranes are listed in Table III. These results indicate that all membranes have a well-developed ionic aggregation inside the clusters. In the case of the irradiated SPEEK membrane, the values of matrix T_g and cluster T_g of the irradiated SPEEK membrane are very similar to that of unirradiated SPEEK membrane, indicating that the ion aggregation of the irradiated SPEEK membrane was not significantly affected by the EB-absorbed dose. On the other hand, the value of matrix T_g was found to be increased with an increase in the crosslinker content since the degree of crosslinking of the irradiated SPEEK/1,4-butanediol membranes increases. Typically, both the matrix and cluster T_g of an amorphous random ionomer depend on the degree of crosslinking. For example, with an increase in the degree of crosslinking, the cluster T_g of amorphous random ionomers increases. However, in the results of Figure 5, the value of cluster T_g decreased with an increase in the crosslinker content. There might be two possible explanations for the decreased cluster T_g with an increase in the crosslinker content.[48,49] The first is the decreased size of ionic aggregation in the irradiated SPEEK/1,4-butanediol membranes owing to the increased uncharged crosslinker. The second is the uncompleted 1,4-butanediol crosslinker to be played as a polar plasticizer in the irradiated SPEEK/1,4-butanediol membranes. When a large amount of uncompleted 1,4-butanediol is located in ionic aggregation, the ion interaction of the ionic aggregation in the membrane decreases. Therefore, the cluster T_g of the membrane decreases. These results will be discussed later in the morphology study of the crosslinked membrane.

The morphology of the crosslinked membranes can be measured by small angle X-ray scattering (SAXS) experiments. Figure 6 shows the SAXS profile of the unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol membranes. It was found that the unirradiated SPEEK membrane and irradiated SPEEK membrane show the position of the maximum peak ($q_{\max}$) at ca. 0.294 Å^{-1}. The $q_{\max}$ of the irradiated SPEEK/1,4-butanediol membranes was shifted to a lower angle compared to the unirradiated SPEEK membrane (Table IV). The value of the Bragg distance between the scattering centers can be calculated using the Bragg equation ($d_{\mathrm{Bragg}} = 2/q_{\max}$) from the value of $q_{\max}$. The Bragg distance was calculated and is also listed in Table IV. The Bragg distance for the crosslinked membrane is in good agreement with the interionic spacing for the membrane previously reported by a number of authors.[20,36,37,50] The similar Bragg distance of the unirradiated SPEEK membrane and irradiated SPEEK membrane indicates that the morphology of SPEEK was not significantly changed by the EB-absorbed dose. The Bragg distance of the irradiated SPEEK/1,4-butanediol membranes increases with an increase in the crosslinker content. The persistence length of ionic aggregation was observed to be $2.87/q^*$, where q^* is the angle at which the SAXS data begin to deviate from the liner extrapolation line in the plot of log[(Intensity)q] versus q^2.[20,51,52] The persistence length of the irradiated SPEEK/1,4-butanediol membranes was evaluated from the SAXS data and is summarized in Table IV. It can be seen that the persistence length of the irradiated SPEEK/1,4-butanediol membranes increases with an increase in the 1,4-butanediol crosslinker content, indicating that the size of ionic aggregation in the irradiated SPEEK/1,4-butanediol membranes increases. In addition, it was observed that the intensity of the

Table IV. The SAXS Data for the Unirradiated/Irradiated SPEEK and Irradiated SPEEK/1,4-Butanediol Membranes

Sample name	q (Å^{-1})	d_{Bragg} (Å)	q^* (Å^{-1})	Persistence length (Å)
Unirrad. SPEEK	0.294	21.4	0.36	8.0
Irrad. SPEEK	0.294	21.4	0.36	7.9
Irrad. SPEEK/diol 10 wt %	0.272	23.1	0.29	10.0
Irrad. SPEEK/diol 20 wt %	0.271	23.2	0.28	10.3
Irrad. SPEEK/diol 30 wt %	0.267	23.5	0.27	10.6
Irrad. SPEEK/diol 40 wt %	0.237	26.5	0.25	11.7

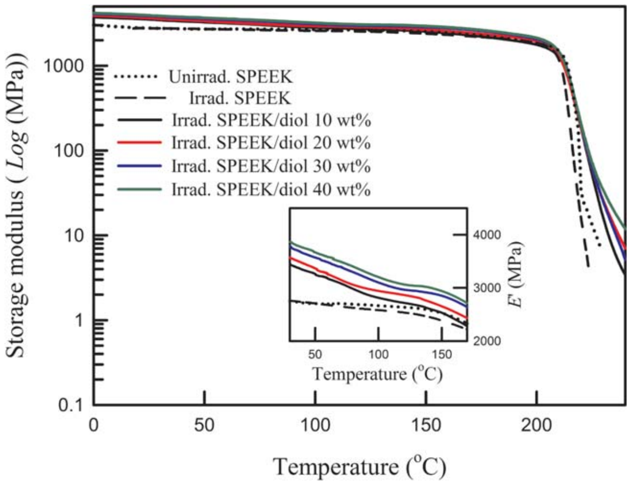

Figure 7. Storage modulus of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes as a function of temperature, measured at 1 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SAXS peak of the crosslinked membranes increased with an increase in the crosslinker content. The increase in the intensity indicates that the number of scattering centers at the most prevalent interionic domain distance increase. It is well known that the number of scattering centers was also dependent on the number of sulfonic acid groups. For example, when the number of sulfonic acid groups in the membrane increases, the number of scattering centers increase. However, the intensity of the SAXS peak in Figure 6 was found to be increased with an increase in the crosslinker content in the membranes although the amount of sulfonic acid in the irradiated SPEEK/1,4-butanediol membrane decreased owing to the increased weight percent of uncharged crosslinker in the crosslinked membranes. It was also found that the SAXS peak width of the crosslinked membranes was increased with an increase in the crosslinker content. Normally, the SAXS peak width represents the homogeneity of the phase of ionic aggregation. For example, the peak width is narrower when the phase becomes more homogenous.[20,51] Therefore, the broad SAXS peak width observed in Figure 6 indicates that the phase of the ionic aggregation became heterogeneous by an increase in the crosslinker content, and the observed heterogeneity is considered to arise from the uncompleted 1,4-butanediol crosslinker which is playing as a polar plasticizer, located in ionic aggregations in the irradiated SPEEK/1,4-butanediol membranes.

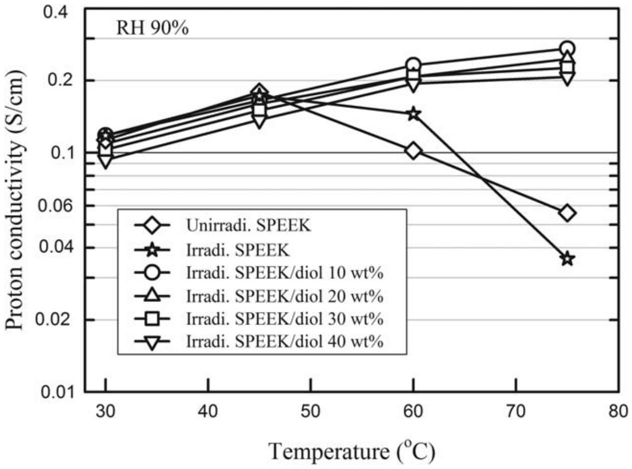

Figure 8. Proton conductivities of the unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes as a function of measured temperature.

Figure 7 shows the storage modulus (E') curve of unirradiated/irradiated SPEEK, and irradiated SPEEK/1,4-butanediol membranes as a function of temperature. It was reported that, with an increasing temperature, the storage modulus for the amorphous random ionomers is changed from a glassy modulus to the glass transition of the matrix phase, the ionic plateau, the glass transition of the cluster phases and then a rubbery modulus. For all membranes, with an increasing temperature, the storage modulus was changed from a glassy modulus to a glass transition, and then to a rubbery modulus. The intermediate region between matrix T_g and cluster T_g is called an ionic modulus.[44] Since the ionic modulus of the unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol membrane was not clearly shown in the storage modulus, the region of the ionic modulus is expanded, as shown in the inset in Figure 7. The values of ionic modulus in Table III show that the ionic modulus increases with an increase in the crosslinker content, implying that the ionic modulus is significantly affected by the crosslinker content. However, no significant change in the ionic modulus was observed from the unirradiated SPEEK membrane or the irradiated SPEEK membrane. The ionic modulus increases with an increase in the crosslinker content, implying that the ionic modulus is significantly affected by the crosslinker content.

Figure 8 shows the proton conductivity of the unirradiated/irradiated SPEEK membranes, and irradiated SPEEK/1,4-butanediol membranes as a function of the measured temperature at 90% RH. The results show that the proton conductivities of all membranes were measured to be higher than 9×10^{-2} S/cm at 30 and 45°C under 90% relative humidity condition. It was also found that the proton conductivity values of the unirradiated SPEEK membrane and irradiated SPEEK membrane decreased from 45 to 75°C while that of the crosslinked membranes increased up to 75°C. Normally, the proton conductivity of the proton exchange membranes is affected by the mobility of the protons and the formation of the ionic cluster network channel in the membrane, which are mainly dependent on the temperature. It is generally known that protons are transported through the cluster network channel in the proton exchange membrane.[44] With an increase in the temperature, the proton conductivity of a proton exchange membrane generally increases owing to the increased mobility of the proton.[53,54] On the other hand, the formation of ionic cluster network channels is also important to determine the proton conductivity of the membrane and appropriate amount of water is required to form well-developed ionic cluster network channels. However, the excessive water in the membrane decreases the proton conductivity owing to the destruction of the ionic cluster network channels. The decreased proton conductivity of the unirradiated

SPEEK membrane and irradiated SPEEK membrane at higher temperature can be attributed to the destruction of the ionic cluster network channels due to the excessively high water uptake as shown in Table II. The increased proton conductivity of the irradiated SPEEK/1,4-butanediol membranes at high temperature indicates that ionic cluster network channels in the crosslinked membrane are maintained at the high-temperature region by inhibiting the uptake of an excessive amount of water. In addition, it was seen that the proton conductivity of crosslinked membranes was decreased with an increase in the crosslinker content. These results are in good agreement with the IEC value and water uptake results in Table II. The IEC and water uptake value of the irradiated SPEEK/1,4-butanediol membranes was found to be decreased with an increase in the crosslinked content since the unchangeable crosslinker content and degree of crosslinking in the irradiated SPEEK/1,4-butanediol membranes increases with an increase in the crosslinker content. These results suggested that the EB-irradiation method applied in this study is useful in the preparation of a crosslinked membrane using a 1,4-butanediol crosslinker.

CONCLUSIONS

Crosslinked SPEEK membranes were prepared through the EB-radiation crosslinking of SPEEK/1,4-butanediol under various irradiation conditions and used as a proton exchange membrane (PEM) for fuel cell applications. The value of the gel fraction for the EB-crosslinked membranes was increased with an increase in the crosslinker content and EB-absorbed dose. It was found that a brittle EB-crosslinked membrane becomes more flexible with an increase in the crosslinker content from the UTM results. It was also found that the water uptake and IEC value are very dependent on the crosslinker content. The DMA data show that the cluster T_g was slightly decreased with an increase in the crosslinker content. The SAXS data show that the Bragg distance and persistence distance of the crosslinked membrane increase with an increase in the crosslinker content. These results suggest that the uncompleted 1,4-butanediol crosslinker acts as a polar plasticizer in the EB-crosslinked membrane. The proton conductivity values of the prepared crosslinked membranes were measured to be higher than 9×10^{-2} S/cm. We believe that the EB-irradiation method can be useful in the prepared SPEEK/1,4-butanediol based crosslinked membrane with an enhanced proton exchange membrane.

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