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Double crosslinked polyetheretherketone-based polymer electrolyte membranes prepared by radiation and thermal crosslinking techniques

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Abstract

Novel one-step preparation of polymer electrolyte membranes without a membrane casting process is achieved by radiation crosslinking of a polyetheretherketone (PEEK) film to prevent dissolution and deformation of the original film in sulfonating solutions. The films crosslinked with doses more than 33 MGy can be effectively sulfonated in a chlorosulfonic solution, resulting in a crosslinked sulfonated PEEK (sPEEK) electrolyte membrane with high proton conductivity comparable to Nafion. Nevertheless, its water uptake was high for application in fuel cells. The thermal treatment was effective for further crosslinking of the membrane; as a result, the water uptake and methanol permeability of the double crosslinked sPEEK membranes drastically decreased, compensating for a slight decrease of proton conductivity. In addition, unlike the traditional cast sPEEK membrane showing the irreversible swelling in hot water, the double crosslinked sPEEK membranes exhibited excellent stability toward 100 °C hot water for more than 200 h without any decrease in proton conductivity, and had the mechanical and thermal properties superior to those of Nafion.

Keywords: Polymer electrolyte membrane; Polyetheretherketone (PEEK); Radiation crosslinking

1. Introduction

A fuel cell using polymer membranes as electrolyte is a promising candidate as a power source for portable, automobile, and stationary applications. Nafion is a commonly used membrane in fuel cells. However, in the operation at high temperatures (above 80 °C) and low relative humidity, Nafion has limited applicability for fuel cells due to its low proton conductivity and high fuel crossover. Furthermore, the high cost is also a big drawback of Nafion for wide applications [1]. These limitations have already stimulated the development of alternative polymer electrolyte membranes with higher fuel cell performance and the lower production cost.

Among the polymer electrolyte membranes being developed, non-perfluorinated aromatic electrolyte membranes have particularly been brought into focus [2]. These aromatic electrolyte membranes are prepared either by sulfonation of super-engineering plastics, such as polyetheretherketone (PEEK) [3–6] and polyethersulfone (PES) [7,8], or by copolymerization of aromatic monomers, at least one of which contains a sulfonic acid group [9–13]. It has been demonstrated that compared with Nafion these aromatic electrolyte membranes have favorable mechanical properties, lower fuel crossover, and lower production cost. Accordingly, the aromatic electrolyte membranes which have these characteristics should be promising electrolyte candidates for application to fuel cells [14].

The PEEK exhibits an excellent combination of properties; i.e., thermal and hydrolytic stabilities, high strength and toughness, wear and abrasion resistance and solvent resistance. A sulfonated PEEK (sPEEK) electrolyte membrane, which is generally prepared by direct sulfonation of commercial PEEK polymer with subsequent membrane casting, inherits many excellent properties from the PEEK, and exhibits proton conductivity as well. However, although the sPEEK membranes with a higher ion exchange capacity

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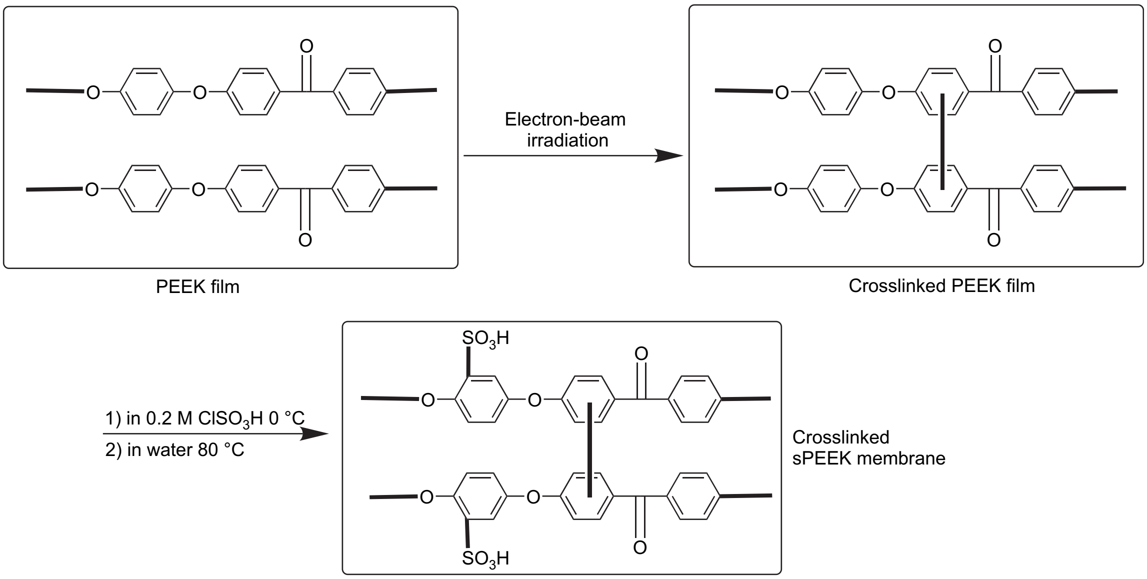
(IEC) (corresponding to a higher sulfonation level) exhibit higher proton conductivity, they also exhibit much higher water and methanol uptake [15−17]. For instance, the sPEEK membrane with an IEC of 2.2 mmol/g loses its shape in hot water after a long-term immersion [17], and the sPEEK membrane with an IEC above 1.6 mmol/g is highly swollen in 1 M of methanol aqueous solution at 80−90 °C [17]. For these reasons, the sPEEK membranes with the IEC above 2.2 and 1.6 mmol/g are not suitable for the hydrogen- and methanol-fed fuel cells, respectively. On the other hand, the proton conductivity of the sPEEK membrane with an IEC below 1.3 mmol/g is much lower than that of Nafion (IEC, 0.91 mmol/g) [2,14,18]. The lower proton conductivity is due to the random distribution of the sulfonic acid groups on an inflexible PEEK backbone, which is not favorable for the formation of proton-conducting networks during the casting of membranes. In most cases, the cast sPEEK membranes with an IEC in the range of 1.4−1.9 mmol/g, were studied as the electrolyte for fuel cells [15−19]. The proton conductivity and water uptake of these membranes are comparable to those of Nafion at room temperature [19]. However, even with a low IEC of 1.4 mmol/g, the sPEEK membranes in hot water above 80 °C show an irreversible drastic swelling, resulting in a gel-like state with limited lifetime in electrolysis system [20−22]. Therefore, crosslinking of the sPEEK membranes may be a reasonable method to avoid the irreversible swelling in hot water, as well as to obtain membranes with high proton conductivity and low water uptake [23−26], Radiation crosslinking techniques have well been employed to restrain the swelling and water uptake of hydrophilic polymers [27]. However, to date, radiation crosslinking has not yet been applied for introducing crosslinking structure into sPEEK electrolyte membranes.

In this study, radiation induced crosslinking was performed on the PEEK films before sulfonation. The optimum irradiation dose on the gel fraction of the PEEK films was investigated. Because the introduced crosslinking structure effectively prevented the dissolution or deformation of PEEK films in the sulfonating solution, a direct film-to-film sulfonation process without membrane casting was established for the preparation of crosslinked sPEEK membranes. The properties of the crosslinked sPEEK membranes were evaluated with respect to the fuel cell applications. Furthermore, thermal crosslinking of the radiation crosslinked sPEEK membrane was carried out to achieve additionally high performance for the membranes.

2. Experimental

The crosslinked sPEEK electrolyte membranes were prepared by radiation induced crosslinking, followed by the direct sulfonation of PEEK films (Scheme 1). The radiation crosslinking not only makes the PEEK films insoluble in the sulfonating solution, but also enhances the mechanical, dimensional and chemical stabilities of the resultant polymer electrolyte membranes.

Radiation crosslinking of the PEEK films (Vitrex® PEEK, 50 μm) were performed at room temperature under air atmosphere with 1 MeV of the accelerating voltage and 10 mA of the electric current using a 60 kW dual-beam type electron accelerator at the Takasaki, Japan Atomic Energy Agency (JAEA) [28,29]. The irradiation dose rate was determined to be 0.67 MGy/min. After irradiation, the PEEK films were thermally treated in a vacuum oven at 120 °C for 24 h for quenching residual radicals and for further crosslinking. Then, the irradiated PEEK films were immersed in a 0.2 M chlorosulfonic acid solution of dichloroethane at 0 °C for sulfonation, washed and kept in hot water at 80 °C for 24 h to convert the formed sulfonyl chloride groups to sulfonic acid groups. The thermal crosslinking of the sulfonic acid groups in the radiation crosslinked sPEEK electrolyte membranes was carried out in vacuum oven at 180 °C for 8 h. The traditional cast



Scheme 1. Process for the crosslinking and sulfonation of PEEK film.

sPEEK membranes were prepared as described in Ref. [30]. That is, 2.0 g of PEEK film was first dissolved in 100 g of 97% sulfonic acid for 3 h at 60 °C under stirring. The resulting solution was poured into 400 g of ice, and thus the sPEEK was obtained, which was then dried and dissolved in *N*-methylpyrrolidone (NMP) for membrane casting. The cast sPEEK membrane was treated by 1 M HCl solution and then washed by distilled water prior to measurement.

The gel fraction was estimated from the weight change of an irradiated PEEK film before and after sulfonation, using the following equation:

$$\text{Gel fraction } (\%) = \frac{W_\mathrm{m} - 80\mathrm{IEC}/1000}{W_\mathrm{f}} \times 100$$

where W_f and W_m are the dry weights of the PEEK film before and after sulfonation. The 80IEC/1000 is the weight of the attached sulfonic acid groups on the PEEK film after sulfonation. The ion exchange capacity (IEC) of the sulfonated PEEK film was determined by acid–base titration [31,32]. The thermal properties were characterized by differential scanning calorimeter (DSC) and thermogravimetric (TG) analysis using the Thermo Plus2 systems (Rigaku, Japan). The specimen (about 5 mg) was heated at a rate of 10 °C/min under the nitrogen flow of 100 ml/min. The degree of crystallinity of PEEK films was calculated from the heat difference between the endothermic and exothermic peaks on the DSC curve, where the heat fusion of fully crystalline PEEK was assumed to be 130 J/g [33]. The tensile tests were carried out according to ASTM D 882, using an STA-1150 universal testing instrument (A&D Co., Ltd, Japan) at a constant crosshead speed of 5 mm/min. The water uptake and proton conductivity of crosslinked sPEEK membranes were measured as described in our previous articles [31,32]. In brief, water uptake was measured by immersing the dry membrane in distilled water at the desired temperature for 24 h. Proton conductivity in longitudinal direction was obtained by impedance spectroscopy measurement using a Solartron 1269 analyzer with an AC perturbation of 0.1 V. During the measurement, the membrane together with electrodes was immersed in distilled water at the desired temperature until the impedance reached steady-state completely (in general more than 1 h). The Attenuated Total Reflectance Fourier Transform Infrared (ATR/FT-IR) spectra were recorded with a FT-IR 710 (Horiba, Japan) equipped with a diamond ATR cell. The methanol permeability of the membranes at 80 °C toward the 10 M of methanol solution was measured as described in literature [34], using a H-type glass apparatus.

3. Results and discussion

3.1. Preparation and physical properties of crosslinked PEEK films

The absorption dose required for crosslinking of PEEK films was first evaluated by the gel fraction of the irradiated films in the sulfonating solution consisting of 0.2 M chlorosulfonic acid in dichloroethane at 0 °C, because one of the main purposes of the crosslinking is to prevent the dissolution or deformation of sPEEK during the sulfonation. The gel fraction of the irradiated films was estimated from the weight change of the crosslinked PEEK films before and after sulfonation, assuming that the uncrosslinked PEEK chains were completely dissolved into the chlorosulfonic acid solution [35,36].

Fig. 1 shows the gel fraction of the irradiated PEEK film as a function of irradiation dose. The PEEK film without irradiation was dissolved in the sulfonating solution within several hours. The PEEK film irradiated with 2 MGy did not keep its shape in the sulfonating solution, and the sulfonated solid material was dissolved in hot water during the subsequent hydrolysis. In contrast, the PEEK films irradiated with doses higher than 33 MGy kept their shapes in the sulfonating solution, indicating the effective formation of crosslinking in the irradiated PEEK films. The gel fraction estimated in this study increased with increase in the irradiation dose, leveling off at about 85% with the dose of 67 MGy. This result was very similar to that reported in the literature, where the gel fraction was measured by an extraction method using trichloroacetic acid as a good solvent [37].

The effective crosslinking of the PEEK film requires a very large irradiation dose, which may also affect the mechanical and thermal properties of PEEK films. The effect of the irradiation dose on PEEK films has been studied for its application in space, nuclear plants, and accelerator facilities, and it has been found that a PEEK film is a radiation resistant material [28,29,37–39]. Thus, the thermal and mechanical properties of PEEK films irradiated with doses up to 100 MGy were measured (Table 1) and compared with those reported in the literatures [28,38,39]. The glass transition temperature (T_g) of the PEEK films slightly increased with irradiation doses of more than 67 MGy, while the degradation temperature gradually

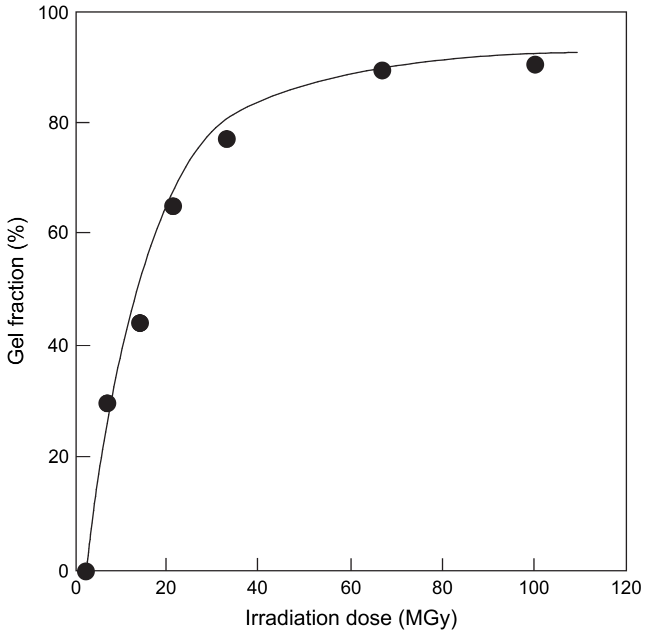


Fig. 1. Gel fraction of the PEEK films as a function of the irradiation dose.

Table 1
Properties of the electron-beam crosslinked PEEK films

Irradiation dose (MGy)	Thermal properties*				Mechanical properties		
	T_g (°C)	T_m (°C)	T_d (°C)	C_{ry} (%)	Stress (MPa)	Elongation (%)	Modulus (GPa)
0	144	343	568	14.6	154	309	2.7
7	142	335	557	12.8	137	278	3.0
14	145	325	553	10.1	113	259	2.7
21	142	315	541	8.3	113	234	2.9
33	145	297	537	2.8	108	186	3.0
67	148	290	526	0.6	84	111	3.2
100	152	–	509	0	79	95	3.1

*T_g, glass transition temperature; T_m, melting temperature; T_d, degradation temperature; C_{ry}, degree of crystallinity, calculated from the DSC curve (heat of fusion of 100% crystallized PEEK, 130 J/g).

decreased with increase in irradiation dose. With increase in irradiation dose, the degree of crystallinity gradually decreased, accompanied by decrease of the melting temperature, and the degree of crystallinity came to be nearly zero with a dose of 67 MGy. On the other hand, the tensile strength and elongation at break decreased with increase in irradiation dose, while the tensile modulus exhibited the tendency to increase in parallel with the irradiation dose. This increase in tensile modulus likely is due chiefly to the crosslinking of the PEEK backbone in the films, which suppresses chain movement and makes the films more rigid [28,29]. On the whole, the irradiation worsened the thermal and mechanical properties of the PEEK films, as previously reported [28,29,37–39]. However, even with high irradiation doses up to 100 MGy the PEEK films retained a high degradation temperature and high mechanical strength compared to the general engineering plastic materials; thus, it should be concluded that the crosslinked PEEK films are suitable as the base films for the preparation of electrolyte membranes for fuel cell applications.

3.2. Properties of crosslinked sPEEK membranes

The crosslinked PEEK films were treated in the sulfonating solution and then hydrolyzed in hot water to convert them into crosslinked sPEEK membranes [31,32]. Table 2 summarizes the properties of the resultant crosslinked sPEEK membranes crosslinked with various irradiation doses and subjected to sulfonation of different durations. The water uptake and proton conductivity were obtained at 25 °C. Nafion was also characterized under the same conditions, which showed the results in good agreement with that reported by DuPont. In the sulfonating solution, the crosslinked PEEK films can swell quickly within 30 min. Therefore, it was possible for the crosslinked PEEK films to be entirely sulfonated. In fact, by means of the energy dispersive X-ray spectroscopy (EDS) measurement, the distribution of sulfonic acid groups on the cross-section of the membrane was confirmed to be uniform even for the membrane with a short sulfonation time of 4 h [34].

Fig. 2 shows the photographs of Nos. 1–6 membranes, which were crosslinked with different irradiation doses and sulfonated with the same time of 24 h. From the appearances of the crosslinked sPEEK membranes, it can be concluded that the higher the crosslinking dose, the better the sPEEK membranes. The sPEEK membrane crosslinked with doses less than 21 MGy was a hydrogel-like material in water (Fig. 2), exhibiting a very low mechanical strength. In this case, the proton conductivity was difficult to measure due to the unstable thickness of the hydrogel-like membrane. The IEC of these crosslinked sPEEK membranes reached 1.9–2.4 mmol/g, about twice that of Nafion (0.91 mmol/g). It was noted that the IEC decreased with the increase in irradiation dose for crosslinking. This can be attributed to the crosslinking structure, which may delay the diffusion of chlorosulfonic acid into the film. By extending the sulfonation duration, the IEC can be enhanced as indicated in the No. 10 membrane. On the other hand, in spite of the decrease in IEC, the proton conductivity of Nos. 4–6 membranes increased. However, it must mention that the IEC is a density of ionic groups in the dry membranes. The membranes with lower crosslinking have a higher IEC but a much higher water uptake. As a result, the density of ionic groups in these water-absorbed membranes was lower, leading to the lower proton conductivity.

The Nos. 4–6 membranes crosslinked with more than 33 MGy irradiation dose exhibited proton conductivity in the

Table 2
Properties of the crosslinked sPEEK membranes

No.	Dose (MGy)	Sulfonation time (h)	IEC (mmol/g)	Sulfonation (%)	Water uptake (%)	Conductivity (S/cm)	Methanol Permeability[b] (10^{-6} cm^2/s)
1	7	24	2.42	89.1	–	–	–
2	14	24	2.38	87.5	1476	–	–
3	21	24	2.27	83.3	1064	–	–
4	33	24	2.19	80.4	512	0.038	–
5	67	24	2.11	77.4	189	0.051	–
6	100	24	1.91	70.2	102	0.069	3.94
7	100	4	1.08	39.6	57	0.027	–
8	100	8	1.68	62.0	72	0.043	–
9	100	30	2.21	81.3	113	0.080	–
10	100	48	2.36	86.6	128	0.081	–
11[a]	100	24	1.69	–	51	0.057	1.97
Nafion	–	–	0.91	–	30	0.060	6.63

[a] The No. 11 was a thermally treated membrane of No. 6.

[b] Measurement conditions, 10 M methanol aqueous solution, 80 °C.

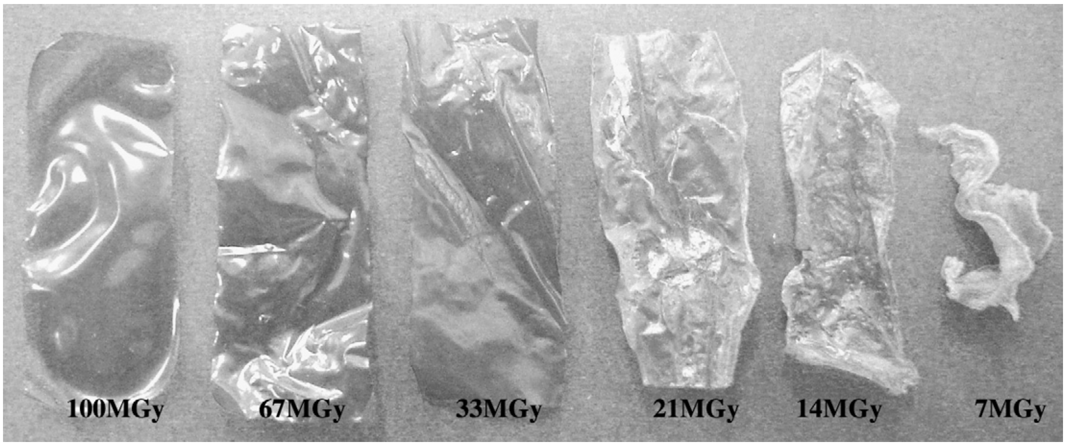


Fig. 2. Photographs of the sPEEK membranes crosslinked with different irradiation doses as inset in figure. Sulfonation time, 24 h.

range of 0.038–0.069 S/cm, comparable to Nafion (0.06 S/cm). However, they exhibited a wide range of water uptake; even the membrane crosslinked with 100 MGy, the water uptake was 102%, which was still higher than that of Nafion (30%). Nevertheless, the 100-MGy crosslinked sPEEK membranes in a water-saturated state have enough mechanical strength for application in fuel cells.

For favorable water uptake, irradiation dose of more than 67 MGy is necessary in a one-step preparation of the crosslinked sPEEK membranes. Also, the water uptake and proton conductivity of the crosslinked sPEEK membranes varied according to their sulfonation levels (amounts of sulfonic acid groups linked to the aromatic rings of PEEK), which in turn were a function of sulfonation time. The Nos. 6–10 membranes are the 100-MGy crosslinked sPEEK membranes sulfonated with different durations. Obviously, both the water uptake and proton conductivity increased with the increase of sulfonation time, and leveled off at near 24 h. Finally the water uptake and proton conductivity of the membrane reached 128% and 0.081 S/cm, respectively, after sulfonation for 48 h.

The water uptake at room temperature of the crosslinked sPEEK membrane was much higher than that of cast sPEEK membranes reported in the literatures [2–6]. For instance, the cast sPEEK membranes with an IEC of about 1.65 mmol/g have the water uptake less than 40% [17,18,40], while the 100-MGy crosslinked sPEEK membranes with the similar IEC of 1.68 mmol/g (No. 8 membrane) showed the higher water uptake of 72%. The lower water uptake of the cast sPEEK membranes was considered to be the result of the lower phase separation between the hydrophilic phase comprising sulfonated PEEK chains and the hydrophobic phase comprising unsulfonated PEEK chains. On the contrary, the formation of hydrophilic phase with the sulfonic acid groups is made possible by the fact that the sulfonation reaction occurs at sulfonation tracks, through which the sulfonating solution can penetrate into the crosslinked PEEK films. Therefore, a more distinct phase separation structure was possible to occur in the membranes, leading to the easy formation of water cluster in water.

3.3. Preparation and properties of double crosslinked sPEEK membranes

Even with the highest irradiation dose (100 MGy), the crosslinked sPEEK membranes have still high water uptake for fuel cell applications. By reducing the sulfonation time, i.e., reducing the IEC, the water uptake could be reduced to be 57% but along with the large decrease of the proton conductivity down to 0.027 S/cm (Table 2, No. 7). In contrast, when the 100-MGy crosslinked sPEEK membrane (Table 2, No. 11) with an IEC of 1.91 mmol/g and a proton conductivity of 0.069 S/cm was thermally treated in vacuum at 180 °C for 8 h, we found that the water uptake drastically decreased from 102% to 51%, compensating for a slight decrease of proton conductivity from 0.069 to 0.057 S/cm, and a decrease of IEC from 1.91 to 1.69 mmol/g. The decreases in the water uptake and IEC indicated additional thermal crosslinking (double crosslinked sPEEK membrane) by conversion of some of the sulfonic acid groups to sulfone structures [2,41].

The FT-IR spectra of the double crosslinked sPEEK membrane are shown in Fig. 3 along with the unsulfonated 100-MGy crosslinked PEEK (cPEEK) film used for comparison. On the double crosslinked sPEEK membrane spectra, new absorption bands at 3500 cm^{-1} assigned to the OH groups, and at 1020, 1077 and 1249 cm^{-1} assigned to asymmetric and symmetric stretching vibrations of O=S=O appeared, indicating the formation of sulfonic acid groups. Since the trisubstitution of aromatic rings after the sulfonation was observed at the absorption band at 1469 cm^{-1}, it is clear that the new sulfonic acid groups attached on the aromatic rings of PEEK [40,42]. The FT-IR spectra of the crosslinked sPEEK membrane and the double crosslinked sPEEK membrane were very similar; thermal crosslinking bonds were difficult to identify in the FT-IR spectra. However, the crosslinked sPEEK membrane obtained in this study was insoluble in organic solvents including NMP even at high temperature; furthermore, the thermal treatment of the crosslinked sPEEK drastically restrained the swelling and water uptake of the membrane. Therefore, it should be concluded that the combination of radiation and thermal crosslinkings is a practical technique for the

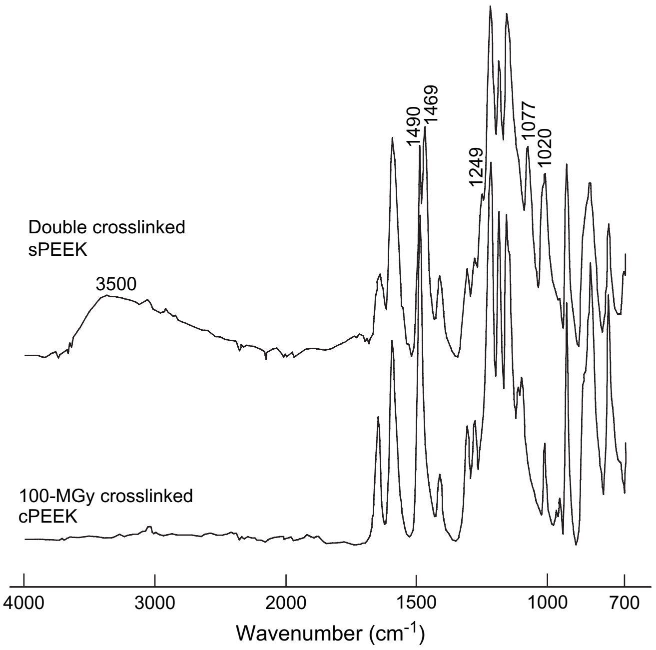


Fig. 3. FT-IR spectra of the double crosslinked sPEEK membrane and 100-MGy crosslinked PEEK film.

preparation of double crosslinked sPEEK membranes with high proton conductivity and low water uptake.

Figs. 4 and 5 show the water uptake and proton conductivity of the double crosslinked sPEEK membrane (IEC, 1.69 mmol/g) as a function of temperature. For comparison, the cast sPEEK membrane with an IEC of 1.65 mmol/g, prepared by the traditional method using 97% sulfonic acid as the sulfonating solution and NMP as the cast solvent, was also measured and the results were plotted in figures. At temperature below 50 °C, both the water uptake and proton conductivity of the cast sPEEK membrane were lower than those of the double crosslinked sPEEK membrane. However, above 50 °C, the cast sPEEK membrane was considerably swollen, reaching a high water uptake of 95.7% and a high proton conductivity of 0.10 S/cm at 60 °C, above which the cast sPEEK membrane in water was irreversible swollen to a gel-like state with the water uptake higher than 1000%, and the proton conductivity cannot be measured because of the break of the membrane in water. On the contrary, the double crosslinked sPEEK membrane was very stable in water, showing the slight increases in both water uptake and proton conductivity with the temperature up to 100 °C. In addition, the water uptake and proton conductivity of the membrane at 100 °C, being 67.2% and 0.11 S/cm, respectively, can be held for a long time more than 200 h in the 100 °C hot water. Therefore, the double crosslinked sPEEK membrane was considerably stable toward hot water.

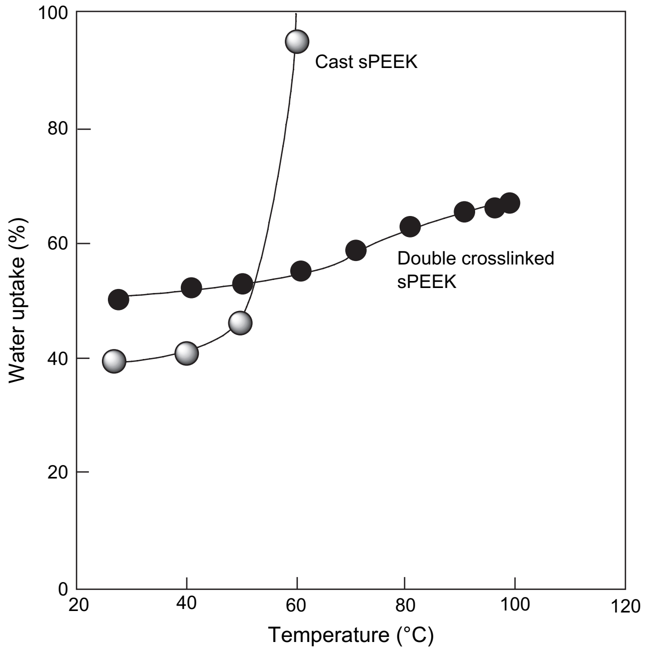


Fig. 4. Water uptake of the sPEEK membranes as a function of temperature.

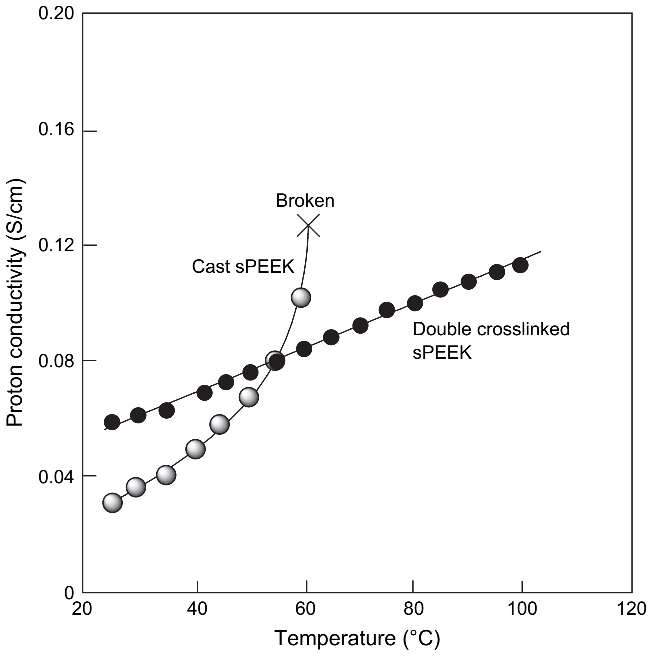


Fig. 5. Proton conductivity of the sPEEK membranes in water as a function of temperature.

Fig. 6 shows the TG profiles of the 100-MGy crosslinked PEEK (cPEEK) film and the double crosslinked sPEEK membrane, which was dried at 80 °C in vacuum for 24 h before the measurement. The 100-MGy crosslinked PEEK (cPEEK) film has a high degradation temperature near 500 °C. The double crosslinked sPEEK membrane has a three-step weight loss; the initial weight loss below 150 °C due to the evaporation of the bound water absorbed in the membrane, the second weight loss starting at about 285 °C mainly attributable to the decomposition of sulfonic acid groups, and the last weight loss near 500 °C due to the degradation of the residual PEEK chains. Since the thermal degradation of the double crosslinked sPEEK membrane occurring at near 285 °C is similar to that of Nafion, the thermal stability was adequate for fuel cell applications. The T_g of the double crosslinked sPEEK membrane measured by DSC was near 224 °C, which was

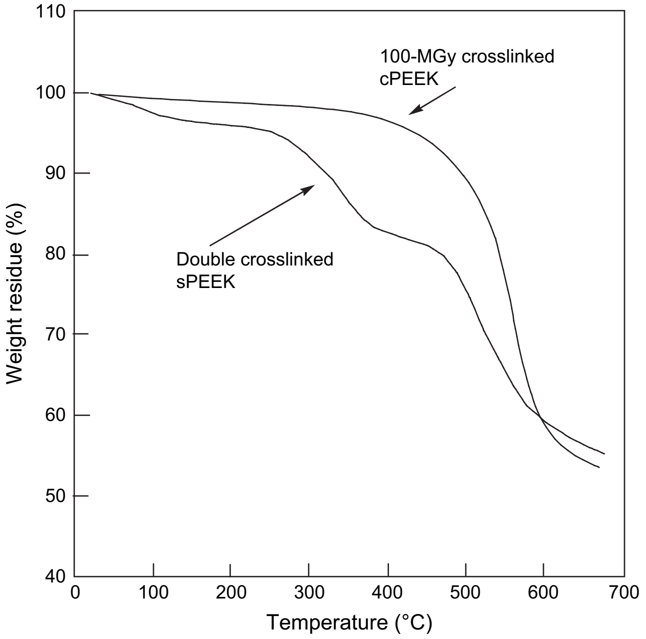


Fig. 6. TG of the double crosslinked sPEEK membrane and 100-MGy crosslinked PEEK film.

considerably higher than 110 °C, the T_g of Nafion. Although further investigation of actual use in a fuel cell, such as long-term fuel cell test, is necessary in order to determine the actual thermal stability of these new electrolyte membranes, the double crosslinked sPEEK membrane likely is an attractive candidate for a polymer electrolyte membrane fuel cell (PEMFC) operating at temperature above 110 °C owing to its high T_g [2].

Mechanical properties also are important parameters for the electrolyte membranes used in fuel cells. The tensile strength–elongation curves (stress–strain curves) of the double crosslinked sPEEK membrane, 100-MGy crosslinked sPEEK membrane and Nafion are shown in Fig. 7. As reported by DuPont, Nafion is very soft and ductile, exhibiting tensile strength of 34.8 MPa and an elongation at break of 294% in this study. In comparison, both the double crosslinked and 100-MGy crosslinked sPEEK membranes possessed quite high tensile strengths (56 and 65 MPa), and adequate elongations at break (58% and 98%). As shown in Fig. 7, after thermal treatment, the tensile strength and elongation at break of the electrolyte membranes decreased, while the tensile modulus and tensile strength at the yield point increased.

The methanol permeability of Nos. 6 and 11 membranes, and Nafion, was determined at 80 °C toward the 10 M of methanol aqueous solution. The traditional cast sPEEK membrane with an IEC of 1.65 mmol/g was dissoluble in the methanol solution at 80 °C, and the methanol permeability cannot be determined. As shown in Table 2, the double crosslinked sPEEK membrane showed a methanol permeability of 1.97×10^{-6} cm^2/s, which was considerably lower than those of the crosslinked sPEEK membrane without thermal treatment (3.94×10^{-6} cm^2/s), and Nafion (6.63×10^{-6} cm^2/s). Therefore, this double crosslinked sPEEK membrane which possesses lower methanol permeability, higher water stability and better proton conductivity, is a promising material for application in fuel cells.

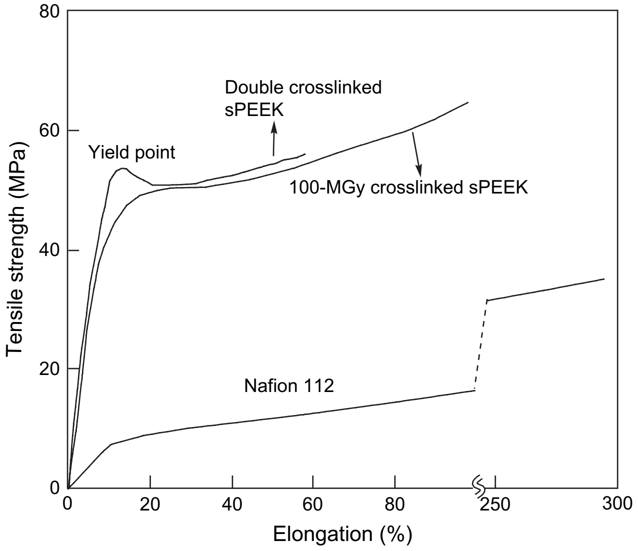


Fig. 7. Mechanical properties of the double crosslinked sPEEK membrane, 100-MGy crosslinked sPEEK membrane, and Nafion.

4. Conclusions

The PEEK films were successfully crosslinked by electron-beam irradiation under air at room temperature. The crosslinked PEEK films reached a high gel fraction of 85% with irradiation dose of above 67 MGy. Although the thermal and mechanical properties of the crosslinked PEEK films somewhat decreased due to the irradiation, they were still comparable to the properties of general engineering plastic materials.

These crosslinked PEEK films do not dissolve and are not deformed while being sulfonated in the sulfonating solution, so that the sPEEK membrane can be directly prepared merely through the sulfonation, without a membrane casting process. The water uptake of the crosslinked sPEEK membrane was strongly dependent on the irradiation dose.

Furthermore, the thermal treatment was effective for further crosslinking of the membrane between the sulfonic acid groups; as a result, the water uptake and methanol permeability drastically decreased, compensating for a slight decrease of proton conductivity. In addition, the double crosslinked sPEEK membrane exhibited higher stability toward 100 °C hot water, higher thermal stability and better mechanical strength. Therefore, it can conclude that the combination of radiation and thermal crosslinkings is a practical technique for the preparation of sPEEK electrolyte membranes, which then exhibit better performance and are a promising material for the application in fuel cells.

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