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A Comparative Study on EB-Radiation Deterioration of Nafion Membrane in Water and Isopropanol Solvents

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Abstract: The purpose of this study was to investigate the influence of electron beam (EB) irradiation on the structure and physical properties of Nafion 117 membranes (in both acid and sodium forms) when they are irradiated in water and isopropanol as solvents. The mechanical properties of Nafion membranes in acid form irradiated in water were found to rapidly deteriorate as the irradiation dose was increased compared to those irradiated in isopropanol. It was also found that the thermal stability of the irradiated Nafion membranes decreased with an increase in the irradiation dose, especially when the Nafion membranes were irradiated in water. It was also observed that the irradiated Nafion membranes in sodium form showed higher mechanical and thermal properties than the irradiated Nafion membranes in acid form regardless of the solvent at the same irradiation dose. The ion exchange capacity of irradiated Nafion membranes was found to be somewhat unaffected compared to the mechanical properties, regardless of the solvent used.

Keywords: EB (electron beam) radiation; irradiation; Nafion

1. Introduction

Nafion is a perfluorosulfonic acid ionomer used mainly in the form of membranes and composed of a hydrophobic perfluorocarbon backbone and vinyl ether side chains terminated with hydrophilic sulfonic acid groups, as shown in Figure 1.

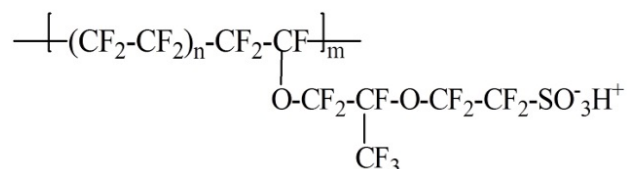
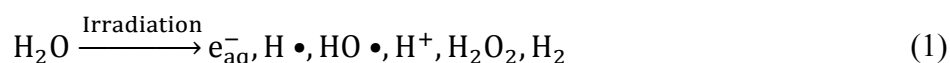


Figure 1. Chemical structure of Nafion in the sulfonic acid form.

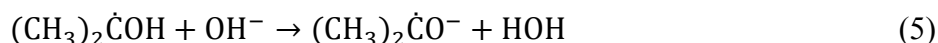
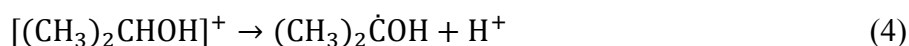
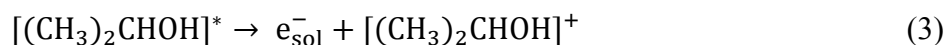
Since the perfluorinated backbone of Nafion has excellent chemical stability, it is widely used as a cell separator in fuel cells, electrolysis cells, batteries, and other electrochemical devices [1]. The sulfonic acid groups of Nafion are very hydrophilic and flexible and form an ionic cluster by combining with water. The water content of Nafion membrane is an important factor that affects its properties. The introduction of water into Nafion membranes leads to the swelling of the membranes by the interaction between the water molecules and ionic groups in the cluster. It has also been reported that Nafion membrane swells more in many organic solvents than in water. In particular, alcoholic solvents such as methanol, ethanol, and isopropanol have a strong affinity for Nafion due to the greater acid strength of the sulfonic acid groups in the alcohol solvent [2–4]. Furthermore, the type of counterion exhibits a distinct influence on the swelling of the Nafion membrane. It has been reported that with the increasing atomic radius of the counterions, the ionic interaction between the sulfonate group and counterions is increased, leading to a reduction in the degree of swelling [5].

As is well known, the fluorocarbon polymer is classified as a typical fragile polymer in a radiation environment since scission of the main chain is easily promoted by irradiation [6]. Several reports describing the radiation durability of Nafion membrane under various irradiation conditions have appeared in the previous literature. These studies indicate that the C–F bonds of Nafion are first broken as a result of EB-irradiation, generating polymer chain free radicals, and these unstable free radicals then cause chain scission reactions. Ultimately, a chain scission caused by EB-irradiation leads to a degradation of the Nafion membrane [6–9]. Balko and Chaklos investigated the effect of electron β and Co^{60} γ -ray radiation on the degradation of Nafion membranes in an air atmosphere [6]. In addition, Iwai *et al.* reported on the radiation degradation of Nafion membranes irradiated with Co^{60} γ -rays or electron beams (EBs) mainly in a water-swollen state [8]. Radiolysis of water generates radicals such as $\text{H}\cdot$ and $\text{OH}\cdot$ in solution as shown below:



Recently, Ghassemzadeh *et al.* reported the degradation mechanism of Nafion membrane by the highly reactive radical species such as $\text{OH}\cdot$ and $\text{H}\cdot$ generated by radiolysis water. In their work, it was found that the $\text{OH}\cdot$ attacks mainly the side chain while the $\text{H}\cdot$ attacks both the main and side chains [9].

Isopropanol has been widely used as a solvent to dissolve Nafion. In addition, it has been often used as an OH• radical scavenger in radiolytic reduction to avoid undesirable oxidation reactions. Previous studies have reported that the radiolysis of isopropanol generates (CH₃)₂ĊOH and (CH₃)₂ĊO[−] as the main intermediates as shown below [10–13]:



As mentioned above, since the solvents water and isopropanol have different radiolysis mechanisms and largely affect the swelling behavior of Nafion membrane, in this study, we investigated the radiation degradation of Nafion 117 membranes (both in acid and sodium forms) swollen in water and isopropanol as solvents. The radiation degradation was studied in terms of the mechanical properties, thermal stability, and ion exchange capacity of the Nafion 117 membrane. The effect on the direct EB-irradiation of Nafion membrane is not considered in this study because many previous studies have reported the results, as mentioned earlier, and identical EB-irradiation conditions were applied to Nafion membranes swollen in water and isopropanol.

2. Experimental Section

2.1. Materials and Sample Preparation

Nafion 117 membrane, 1100 g equivalent weight and approximately 0.177 mm (0.07 inches) thick, was purchased from DuPont Corp. (Wilmington, DE, USA). Hydrogen peroxide (H₂O₂, 30% in H₂O), sulfuric acid (H₂SO₄, 97%), sodium chloride (NaCl), and isopropanol (IPA) were purchased from Showa Company (Gyoda, Japan). Deionized water was obtained using a Wellix Pure II deionizer (MDM Instruments Co., Ltd., Suwon, Korea). The purchased Nafion membrane was pretreated by a conventional process, heating it in a 5 wt% aqueous H₂O₂ solution for 1 h at 80 °C, followed by rinsing in deionized water for 1 h at 80 °C. To assure the complete protonation of the Nafion membrane (Nafion H⁺), the membrane was treated in a 0.5 M aqueous H₂SO₄ solution for 1 h at 80 °C followed by rinsing twice in deionized water for 1 h at 80 °C. Nafion membrane in sodium form (Nafion Na⁺) was obtained by soaking the pretreated Nafion H⁺ membrane in a 1 M aqueous NaCl solution for 24 h at room temperature, followed by rinsing in deionized water twice for 1 h at room temperature. The pretreated Nafion membranes (both acid and sodium forms) were kept in deionized water or isopropanol at room temperature for 1 day prior to the EB-irradiation experiments.

2.2. Irradiation

The Nafion membrane EB-irradiation experiments in a solvent are illustrated in Figure 2. The Nafion membrane was cut to a size of 5 cm × 10 cm and soaked in a square Petri dish (125 mm × 125 mm × 20 mm) containing 115 mL of deionized water or isopropanol. The height of the solvent in a Petri dish was measured as about 1 cm. The samples in the square Petri dish were then

irradiated at room temperature with an electron beam from the electron beam linear accelerator (10 MeV, 0.5 mA) at the Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute (Jeongup, Korea), at irradiation doses ranging from 50 to 800 kGy with a dose rate of 6 kGy/min. After the irradiation, the Nafion membranes were washed with deionized water or isopropanol and then dried in a vacuum oven at 70 °C for 12 h.

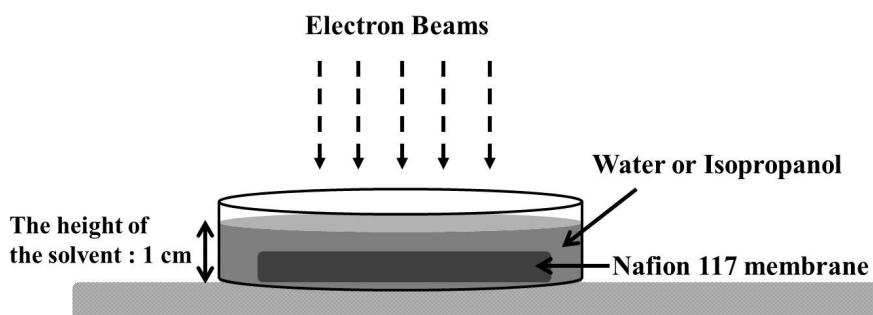


Figure 2. Irradiation of Nafion membrane soaked in a solvent with an electron beam (10 MeV, 0.5 mA).

2.3. Mechanical Property

The mechanical properties of the irradiated/unirradiated Nafion membranes were determined using an Instron model 4400 universal testing instrument (Instron Co. Ltd., Copiague, NY, USA) at a constant crosshead speed of 50 mm/min at room temperature according to the ASTM D638. Samples were cut into 53 mm × 31 mm strips using a precision double blade Film/Fiber cutting instrument (TA Instrument Co. Ltd., New Castle, DE, USA). The thickness of the membranes was determined as the average of three random positions of the membrane samples using a digital thickness gage (Mitutoyo, Kawasaki, Japan).

2.4. Thermal Analysis

Thermogravimetric analysis (TGA) of the irradiated Nafion membranes was carried out with a TGA Q 500 system (TA Instrument Co. Ltd.) under a nitrogen atmosphere to prevent the oxidative thermal degradation of the sample. The samples were placed in a TGA specimen pan and heated at a rate of 10 °C/min in a temperature range of 50 to 600 °C.

2.5. Ion Exchange Capacity

Ion exchange capacity (IEC) of the irradiated Nafion membranes was measured using an acid-base back-titration method. The dried membranes were soaked in a 1 M NaCl solution overnight at room temperature to replace H⁺ ions of the membranes with Na⁺ ions. The solution containing H⁺ ions released from the sample was then titrated with 0.1 M NaOH using an automation titrator (DLL22, Mettler Toledo Company, Greifensee, Switzerland). The IEC values were calculated using the following equation:

$$IEC_{exp} = [0.1 \times V_{NaOH}] / W_{dry} \quad (6)$$

where V_{NaOH} is the volume of 0.1 M NaOH aqueous solution consumed for the volumetric titration and W_{dry} is the dry weight of the membrane, respectively.

2.6. Solvent Uptakes and Thickness Measurement

Nafion membranes (in both acid and sodium forms) were immersed in water and isopropanol at room temperature for 24 h, respectively. The swollen membranes were taken out, and the solvent adhered on the surface of the membranes was wiped off with absorbent paper before weighing. The solvent uptakes were calculated using the following equation:

$$\text{Solvent uptake (\%)} = \left[\frac{(W_w - W_d)}{W_d} \right] \times 100 \quad (7)$$

where W_w and W_d are the weights of the swollen and dried membranes, respectively.

The thickness of the swollen Nafion membranes was measured using a digital thickness gage (Mitutoyo).

3. Results and Discussion

3.1. Mechanical Properties

Nafion membrane belongs to the class of perfluorinated ionomers and is composed of a hydrophobic polytetrafluoroethylene (PTFE) main chain and perfluorinated pendant side chains terminated with hydrophilic sulfonic acid groups [4,8,14]. The PTFE is classified as a typical fragile polymer under a radiation environment since main chain scission is easily promoted by irradiation [6,15]. Hence, in this study, the degradation behavior of the EB-irradiated Nafion membranes in water and isopropanol was evaluated by measuring the elongation at break and the tensile strength of the irradiated Nafion membranes.

Figure 3A,B show the elongation at break and the tensile strength of the EB-irradiated Nafion membranes (both acid and sodium forms) in water and isopropanol. The degree of elongation and tensile strength of the irradiated Nafion membranes were found to be significantly decreased with an increase in irradiation dose. The decreased mechanical properties observed from Figure 3A,B indicate that the EB-irradiation of Nafion membranes led to the main chain scission of the irradiated Nafion membrane and this finally ended up decreasing the mechanical properties. It was also observed that the Nafion membranes swollen in water and isopropanol showed different elongation at break and tensile strength. It is known that Nafion membrane shows different swelling properties in accordance with the solvent and counterions [3,5,16,17]. The ionic groups of the Nafion membrane are aggregated in a perfluorinated polymer matrix to form a network of clusters. The introduction of water into the Nafion membranes leads to the swelling of the membranes by the interaction of the water molecules and ionic groups in the cluster [17–19]. It is also known that the Nafion membrane exhibits a higher swelling in alcohol solvents such as methanol and isopropanol than in water owing to the strong affinity between the perfluorinated ionomer and the alcohol [2–4]. In this study, the water and isopropanol uptakes of Nafion 117 membrane were measured as 23% and 60%, respectively, while the thicknesses in water and isopropanol were determined to be 194 and 234 μm , respectively. Figure 3A,B show that the Nafion membrane swollen in isopropanol has a higher elongation at break with a lower tensile strength compared to that in water. These results indicate that the morphology of Nafion membrane, for examples,

the ionic cluster and crystallinity, are greatly influenced by the solvents, even after the drying process, finally resulting in a difference in the mechanical properties [1].

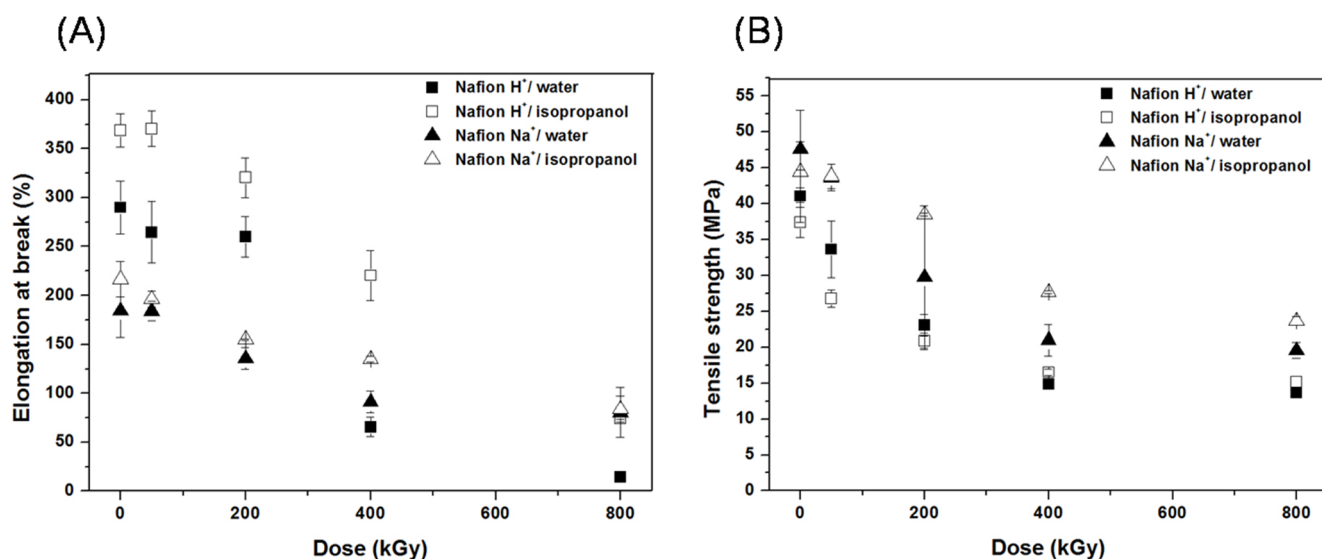


Figure 3. Mechanical properties of EB-irradiated Nafion membranes (both acid and sodium forms) in water and isopropanol solvent: **(A)** Elongation at break; **(B)** Tensile strength.

Figure 3A,B show that the mechanical properties of the Nafion membranes are also affected by the counterion. Nafion membrane in sodium form (Nafion Na⁺) exhibited a lower elongation at break and a higher tensile strength compared to Nafion membrane in acid form (Nafion H⁺). It is known that with the increasing atomic radius of the counterions, the ionic interaction between the sulfonate group and counterions is increased [5,19], thus a higher tensile strength and lower elongation at break were observed from the Nafion Na⁺. Figure 3A,B also show that with increasing EB-irradiation doses, the mechanical properties (both elongation at break and tensile strength) of the Nafion membranes were significantly decreased, regardless of the solvent and counterion. In particular, the elongation at break of the Nafion H⁺ irradiated in water was found to be more rapidly decreased than that irradiated in isopropanol, especially when the dose increased to 400 from 200 kGy. It can be seen that the radiolysis of water was promoted by EB-irradiation after 200 kGy of irradiation. This result implies that the solvents can influence the main chain scission of Nafion membrane during EB-irradiation despite the fact that the main chain scission is considered to be largely caused by the free radicals on the main chain generated by direct contact between the main chain and EB [6,20,21]. It is known that the radiolysis of water by high-energy radiation produces highly reactive species such as H•, OH•, and electrons along with H⁺, H₂O₂, and H₂ in an aqueous solution. The solvated electrons and H• are strong reducing agents, whereas OH• radicals are a strong oxidizing agent. In the radiolysis of isopropanol by high-energy radiation, (CH₃)₂ĊOH and (CH₃)₂ĊO[−] are known to be produced as the main intermediates [10–13]. The rapid decrease in the elongation at break of Nafion H⁺ irradiated in water means that a large quantity of highly reactive species including H• and OH• are present in water after EB-irradiation, resulting in the chain scission of Nafion. It was also observed that the elongation at break of the Nafion H⁺ irradiated in water was rapidly decreased compared to that of Nafion Na⁺ in the same water solvent. This can be attributed to the higher water swellability of Nafion H⁺ than Nafion

Na⁺ [5,19]. Consequently, Nafion H⁺ irradiated in water can be affected more by the highly reactive species generated during the radiolysis of water than Nafion Na⁺ since they contain more water.

3.2. Thermal Analysis

Figure 4A,B show the TG curves of the EB-irradiated Nafion H⁺ in water and isopropanol. The TGA curves were obtained under a nitrogen atmosphere. The thermal stability of the Nafion membranes irradiated in water and isopropanol was found to gradually decrease with an increase in the irradiation dose.

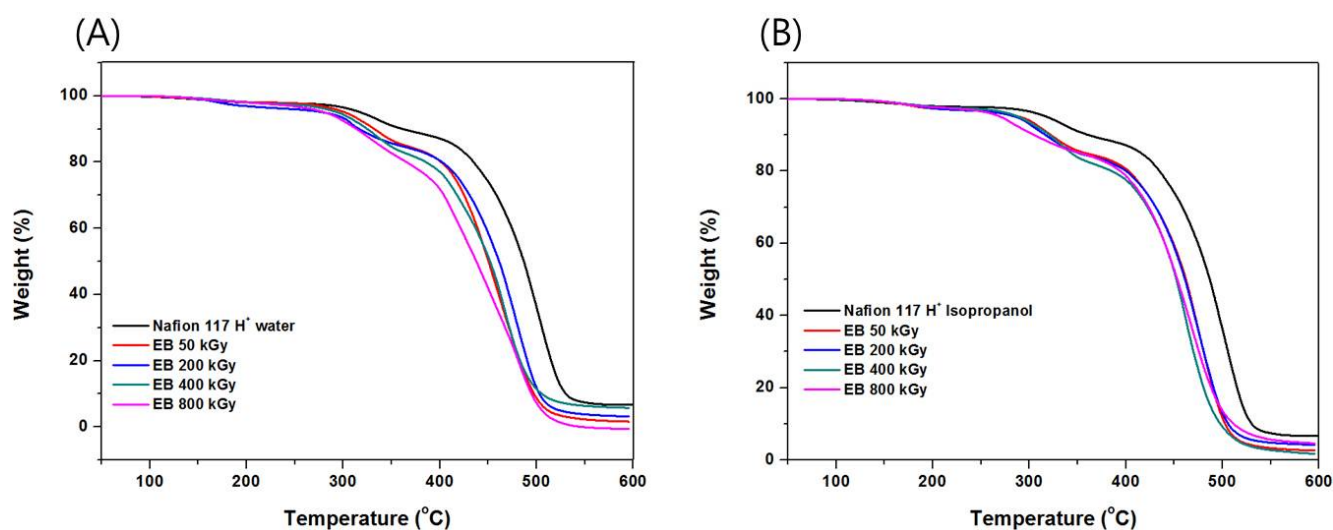


Figure 4. TG curves of EB-irradiated Nafion membranes in acid form under a N₂ atmosphere: (A) in water; (B) in isopropanol solvent.

According to the previous morphological studies, Nafion has a phase-separated structure that consists of a crystalline domain of hydrophobic PTFE main chains and an ionic domain of hydrophilic side chains. The shift of the thermal degradation temperature to a lower temperature region is considered due to the main PTFE chain scission of the Nafion membranes by EB-irradiation [6,14,15]. It is also known that Nafion H⁺ undergoes a three-stage decomposition process, as shown in the TG curves. The first stage is due to the evaporation of the solvent. The second and third stages can be attributed to desulfonation and main chain degradation, respectively [22,23]. It was observed that the thermal stability of the Nafion H⁺ irradiated in water was decreased more with an increase in irradiation dose compared with that irradiated in isopropanol. This result indicates that the solvent used in the EB-irradiation also affects the thermal stability of the EB-irradiated Nafion H⁺ by involving the main PTFE chain scission as observed in the mechanical study of the EB-irradiated Nafion membrane in Figure 3.

Figure 5A,B show the TG curves of the EB-irradiated Nafion Na⁺ in water and isopropanol. The TG curves exhibit different profiles from those of Nafion H⁺ shown in Figure 4. It is known that Nafion Na⁺ has a higher thermal stability than Nafion H⁺ owing to the strong ionic interaction between SO_3^- and Na⁺ that stabilizes the C–S bond [23–28]. Therefore, the sulfonate groups in the Nafion membranes in sodium form seem to be stable until the PTFE main chains are thermally decomposed. In the case of the thermal stability of the EB-irradiated Nafion Na⁺, the thermal stability of the Nafion

Na^+ irradiated in water was decreased more with an increase in irradiation dose compared with those irradiated in isopropanol, as observed in the case of Nafion H^+ in Figure 4.

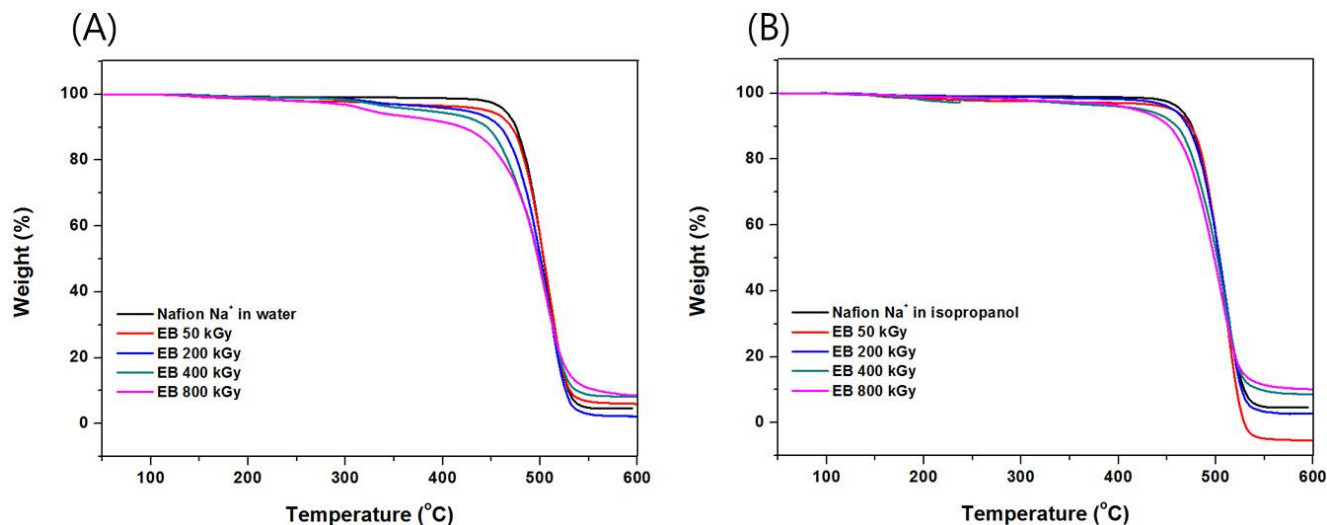


Figure 5. TG curves of EB-irradiated Nafion membranes with sodium form under a N_2 atmosphere: (A) in water; (B) in isopropanol solvent.

3.3. Ion Exchange Capacity

The ion exchange capacity (IEC) of ionomers such as Nafion is an important factor to dominate the overall property of the ionomers. Figure 6 shows the ion exchange capacity of the EB-irradiated Nafion membranes (both acid and sodium forms) in water and isopropanol at room temperature [8].

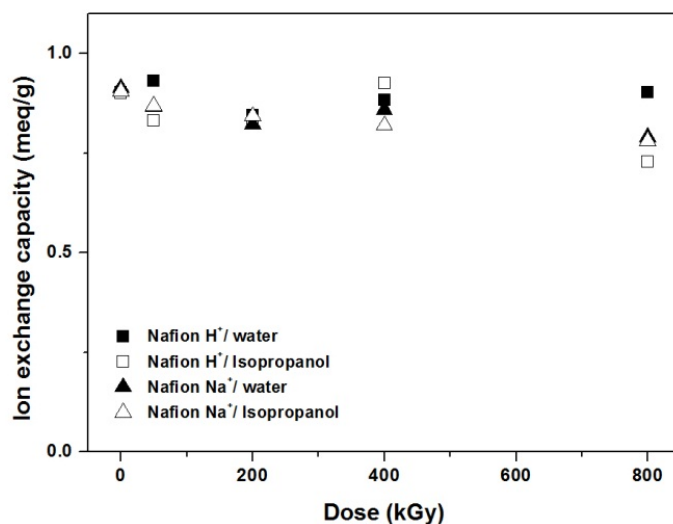


Figure 6. Ion exchange capacity of EB-irradiated Nafion membranes (both acid and sodium forms) in water and isopropanol.

It was observed that the ion exchange capacity of the Nafion membranes remained rather constant as the irradiation dose increased. No significant effects of the counterions and the solvent on the ion exchange capacity of the EB-irradiated Nafion membranes were observed under the irradiation conditions, even though the hydroxyl radicals produced in the radiolysis of water are reported to cleave the side

chains containing a sulfonic acid group [9]. Considering this result together with the radiation degradation behavior of the mechanical properties under EB-irradiation shown in Figure 3, it can be concluded that the radiation degradation of the side chain of Nafion membranes by EB-irradiation occurred more slowly than the main chain degradation without significant effects of the solvent or counterions.

4. Conclusions

In this study, the influence of EB-irradiation on the structure and physical properties of Nafion 117 membranes (both acid and sodium forms) soaked in water and isopropanol was investigated. The results indicate that the Nafion membrane swollen in the isopropanol has a higher elongation at break along with a lower tensile strength compared to those in irradiated water due to the higher swelling in the isopropanol solvent. It was also observed that the Nafion Na⁺ has a higher tensile strength and lower elongation at break than Nafion H⁺ since the ionic interaction between the sulfonate group and counterions is increased as the atomic radius of the counterions increases. With an increase in the EB-irradiation dose, the mechanical properties of the Nafion membranes were significantly decreased regardless of the solvent and counterions. In particular, the mechanical properties of Nafion H⁺ irradiated in water were found to rapidly decrease compared with other membranes due to the OH• and H• radicals generated in the water by radiolysis. The radiation effect on the thermal stability of the Nafion membranes shows a similar tendency as the mechanical properties. It was observed that the Nafion Na⁺ has a higher thermal stability than the Nafion H⁺, and the thermal stability of Nafion membranes irradiated in water was rapidly decreased with an increase in the irradiation dose, compared with those irradiated in isopropanol. On the other hand, the ion exchange capacity of the Nafion membranes was found to be somewhat maintained with an increase in the irradiation dose. No significant effects of the counterions and the solvent on the ion exchange capacity of the EB-irradiated Nafion membranes were observed under the irradiation conditions. This result means that the radiation degradation of the side chain of the Nafion membranes occurred more slowly than that of the main chain under EB-irradiation without any significant effects of the solvent and counterions.

Acknowledgments

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Author Contributions

Junhwa Shin and Joon-Yong Sohn designed and directed the experiments. Ji Sun Choi conducted the experiments and wrote this manuscript as well.

Conflicts of Interest

The authors declare no conflict of interest.

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