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Simple and Quick Preparation of Cation Exchange Membrane Using Electron Beam Irradiation

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1. Introduction

Ion exchange membrane as semi-permeable membrane, which transports certain dissolved ions while blocking countparts, has been widely used as electrodialysis, seawater desalination, industrial wastewater treatment, food production, and development of renewable energy sources [1]. However, preparation methods of ion exchange membrane such as polymeric backbones prepared by either post-functionalization of polymers or direct polymerization of functionalized monomer, are so complicated. Also, ion exchange membrane with high ion exchanges capacity generally have high water uptake and then deteriorate dimensional stability and mechanical strength. In this study, we intended to fabricate the crosslinked cation exchange membrane with high ion exchange capacity and an appropriate water uptake by quick and simple electron beam irradiation-induced crosslinking.

2. Methods and Results

2.1 Materials

Poly(sodium-4-styrenesulfonate) (FSPSNa) (M_w 1,000,000) with 100 mol% ion exchangeable functional group (sulfonic acid), poly(vinyl alcohol) (PVA), glycidyl methacrylate (GMA) and, dimethyl sulfoxide (DMSO) were supplied by Sigma-Aldrich Co. (USA). Substituted PVA (SPVA) which can be crosslinking by electron beam irradiation was synthesized using trans-esterification reaction of PVA with GMA in DMSO without catalyst [2].

2.2 Preparation and characterization of Cation Exchange Membrane

The preparation of crosslinked FSPSNa/SPVA cation exchange membranes via solution casting and subsequent electron beam irradiation were described as Fig. 1.

FSPSNa and SPVA with 10 mol% substitution degree were dissolved in DMSO to for a 10 wt% solution (the weight ratio of FSPSNa to SPVA was set to 50/50, 40/60, and 35/65) and then the solution casted on glass plates using a doctor blade. Afterwards, the resulting FSPSNa/SPVA membranes were dried in a vacuum oven for 6 h at 70 °C to remove the remaining DMSO. Electron beam irradiation of the prepared membranes were performed under nitrogen atmosphere at room temperature with an ELV-8 electron accelerator at a voltage of 1.5 MeV in EB Tech Co., Ltd. (Daejeon, Korea). The cation exchange membranes were irradiated to doses of 50, 100, and 200 kGy, respectively. The electron beam current was 7.2 mA and the dose rate was 10 kGy per pass.

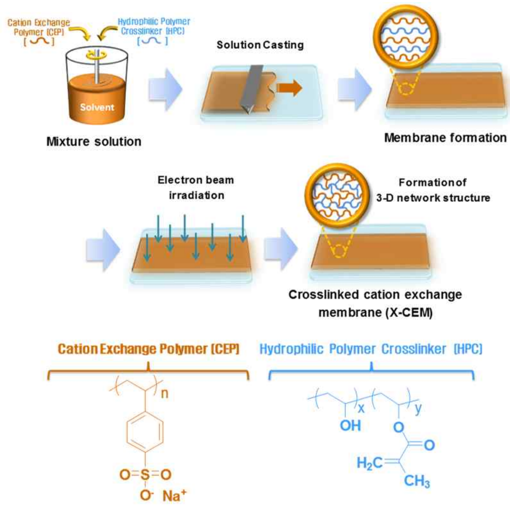

Fig. 1. Preparation of crosslinked cation exchange membranes via solution casting and subsequent electron beam irradiation.

The properties of the prepared FSPSNa/SPVA membranes were characterized by diverse experiments such as gel fraction, water uptake, ion exchange capacity, area resistance and thermal stability.

2.3 Gel-Fraction

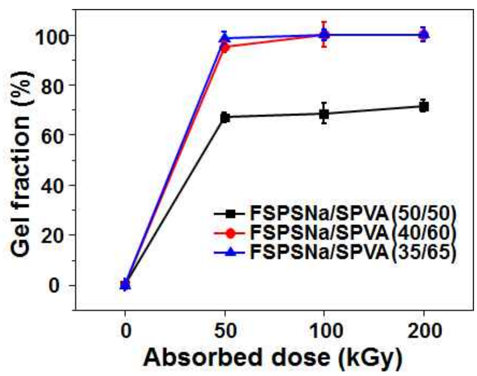

Fig. 2. Gel-fraction of FSPSNa/SPVA cation exchange membranes at various composition and absorbed doses

To confirm the introduction of crosslinked structure in the electron beam(EB)-irradiated cation exchange membranes, the gel fraction was quantified by measuring the weight of the insoluble part before and after the extraction using the DMSO as a good solvent for the FSPSNa and SPVA and the results were represented as Fig 2. The gel fraction is calculated from the following equation:

$$\text{Gel fraction (\%)} = \frac{W_d}{W_i} \times 100 \quad (1)$$

where W_i and W_d are the weight of the dried membrane before and after solvent extraction, respectively [3].

As shown in Fig. 2, the gel fraction of FSPSNa/SPVA cation exchange membranes without electron beam irradiation was dissolved in DMSO within several hours. However, FSPSNa/SPVA cation exchange membranes with above 60 wt% SPVA showed the gel frication of about 100%, indicating that the SPVA in the prepared cation exchange membranes was completely crosslinked by electron beam irradiation at absorbed dose of above 50 kGy.

2.4 Water uptake

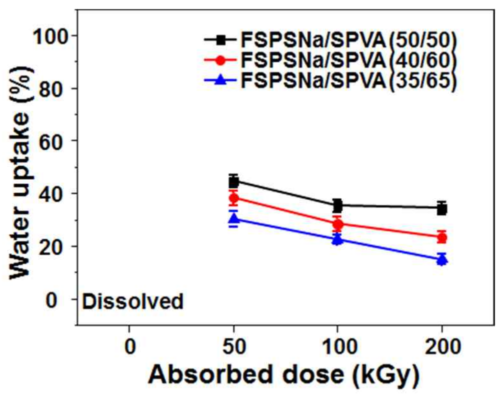

Fig. 3. Water uptake FSPSNa/SPVA cation exchange membranes at various composition and absorbed doses

The water uptakes of the FSPSNa/SPVA cation exchange membranes prepared with various compositions of FSPSNa/SPVA and absorbed doses were measured after the prepare membranes were swelled at 50 °C in deionized water for 7 days. The water uptake value was calculated using the following equation:

$$\text{Water uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s is the weight of the wet membrane and W_d is the weight of the dried membrane [3].

Fig. 3 illustrates the water uptake of FSPSNa/SPVA membranes as a function of absorbed doses and FSPSNa/SPVA composition. Water uptake of the non-EB-irradiated membranes with all composition could not be measured because they were completely dissolved. However, the EB-irradiated membranes were not dissolved. As shown in Fig.3, the water uptake of the EB-crosslinked FSPSNa/SPVA decreased with the increase in SPVA polymer crosslinker contents and in absorbed doses due to the formation of the crosslinked structure in the membranes as gel-fraction results.

2.5 ATR-FTIR

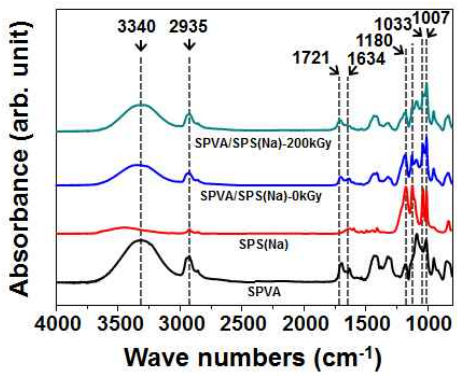

Fig. 4. Fraction of counts lost with voltage and charge sensitive preamplifiers as a function of the true count rate.

To investigate the changes in the chemical structure of the FSPSNa/SPVA cation exchange membranes after electron beam irradiation, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Tensor 37, Bruker Co.) was performed and the results are shown in Fig. 4. Before electron beam irradiation, the specific peaks for FSPSNa/SPVA contained the main peaks for SPVA polymer presented at 3340 (-OH), 2934 (-CH), 1721 (C=O of ester group), 1634 (C=C), 1260(C-O-C), and, 1180(C-O of ester group) cm^{-1} and for FSPSNa presented at 1033 and 1007 cm^{-1} (SO_3^-). After electron beam irradiation at 200 kGy, a specific peak at 1579 assigned to C=C disappeared. This change in chemical structure indicated that the crosslinked structure in FSPSNa/SPVA cation exchange memgbrane was introduced by electron beam irradiation

2.5 Ion Exchange Capacity and Membrane Area Resistance

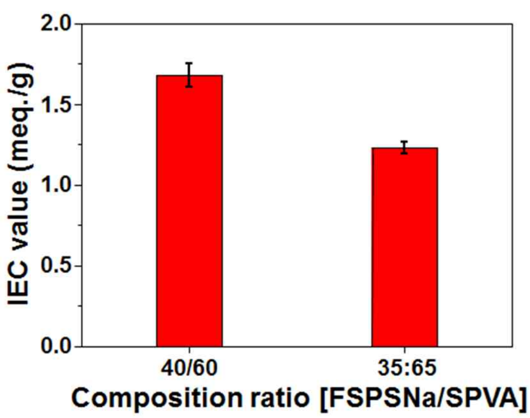

Fig. 5. Water uptake FSPSNa/SPVA cation exchange

membranes at various composition and absorbed doses

The ion exchange capacity (IEC) indicates the content of the ion exchange groups in the ion exchange membrane and is known to significantly affect the ability of ions transfer. IEC was measured using a titration method and was illustrated in Fig. 5. IEC decreased with the increase in the content of SPVA due to the decrease in FSPSNa content with sulfonic acid group and the introduction to crosslinking structure. However, the Fig. 6 showed that FSPSNa/SPVA (40/60) membrane irradiated at 200 kGy had good ion exchange capacity of 1.68 meq/g.

2.6 Thermal property.

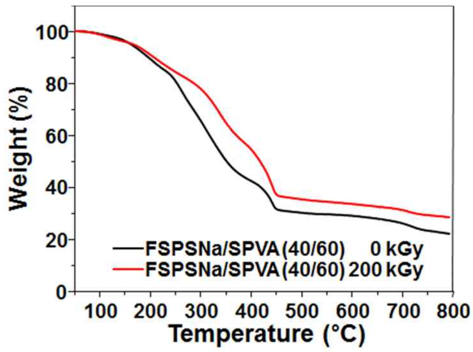

Fig. 6. TGA curves of FSPSNa/SPVA(40/60, w/w) membranes before and after electron beam irradiation at 200 kGy

To investigate the crosslinking effect on the thermal stability of the irradiated FSPSNa/SPVA (40/60) membranes, the TGA analysis was carried out, and the results are shown in Fig. 6. TGA analysis showed that the graph profile of the EB-irradiated membrane shifted to high temperature compared to that of the non-EB-irradiated one. This result confirms that network structures are formed in FSPSNa/SPVA (40/60) cation exchange membrane by EB-irradiation.

3. Conclusions

The crosslinked FSPSNa/SPVA cation exchange membranes with high ion exchange capacity and an appropriate water uptake have been successfully prepared at room temperature by quick and simple electron beam irradiation-induced crosslinking. Based on the results of gel fraction, changes of the chemical structure, and water uptake in the prepared membranes, FSPSNa/SPVA cation exchange membranes were successfully crosslinked by electron beam irradiation. Compared with non-irradiated FSPSNa/SPVA membranes, the thermal stability of EB-irradiated FSPSNa/SPVA membrane was improved from TGA results. The membrane prepared with the composition of FSPSNa/SPVA (40/60, w/w) and at absorbed dose of 200 kGy exhibited the high ion exchange capacity in spite of their lower water uptake, compared to the non-irradiated membrane because of the use of 100 mol% FSPSNa polymer and EB-crosslinkable SPVA.

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