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# Preparation and Characterization of Crosslinked Anion Exchange Membrane Using Electron Beam Irradiation

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**Abstract - The novel crosslinked anion exchange membrane with a high ion exchange capacity and stability was fabricated through a room temperature and solid-state radiation processing. The anion-exchange membrane was prepared by solution casting method at the different compositions of poly(diallyldimethylammonium chloride) and PVA substituted with methacryloyl group, and subsequently irradiated by electron beam to form 3D-network structure. From the various analytical results, the 3D-network crosslinked anion-exchange membrane exhibited not only a high ion exchange capacity ($>1.7\ meq \cdot g^{-1}$) but a superior water stability (water uptake $\leq 30\%$) through a room temperature and quick radiation crosslinking process. Also, the prepared anion exchange membrane had better thermal stability compared to non crosslinked anion exchange membrane (control).**

**Key words : Electron beam irradiation, Crosslinking, Methacryloyl-substituted polyvinyl alcohol, Anion exchange membrane**

## INTRODUCTION

Anion exchange membrane (AEM) containing positively charged groups, such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$, $-SR_2^+$, etc., is semi-permeable membrane, which transports certain dissolved anions while blocking cations (Nasef and Ujang 2012; Varcoe *et al*. 2014). AEM has been used extensively in industrial applications due to its selectivities for specific ions including the electrodialysis, seawater desalination, industrial wastewater treatment, food production, alkaline fuel cell and various other purposes (Strathmann 2010; Strathmann *et al*. 2013; Ran *et al*. 2017).

AEMs have been fabricated using various preparation methods, generally including polymerization of monomers, at least one of which contain cationic group, introduction of cationic group into a polymer, and polymer blends containing the polymer with 100 mol% cationic groups and the polymer with film-forming and crosslinkable capacity (Karidurganavar *et al*. 2006; Zhang *et al*. 2013). Among the methods, polymer blending method is simple and provides the potential for combing the attractive features of each blend component while at the same time reducing their deficient characteristics. However, even AEMs prepared by above-mentioned methods have problem of deterioration of dimensional stability due to excessive water swelling.

Crosslinking is an effective procedure to improve dimensional stability of AEM (Wang *et al*. 2012; Maurya *et al*. 2013). Crosslinking method commonly requires crosslinking agents, long-processing time, and high temperatures. Therefore, there is still high demand for a cross-linking method that occurs at room temperature, and is also quick, cost-effective, and scalable.

The electron beam technique has been considered as a promising crosslinking procesure for introduction of 3-D network structure in AEM. Unlike conventional crosslinking, this radiation processing offers several clear advantages in-

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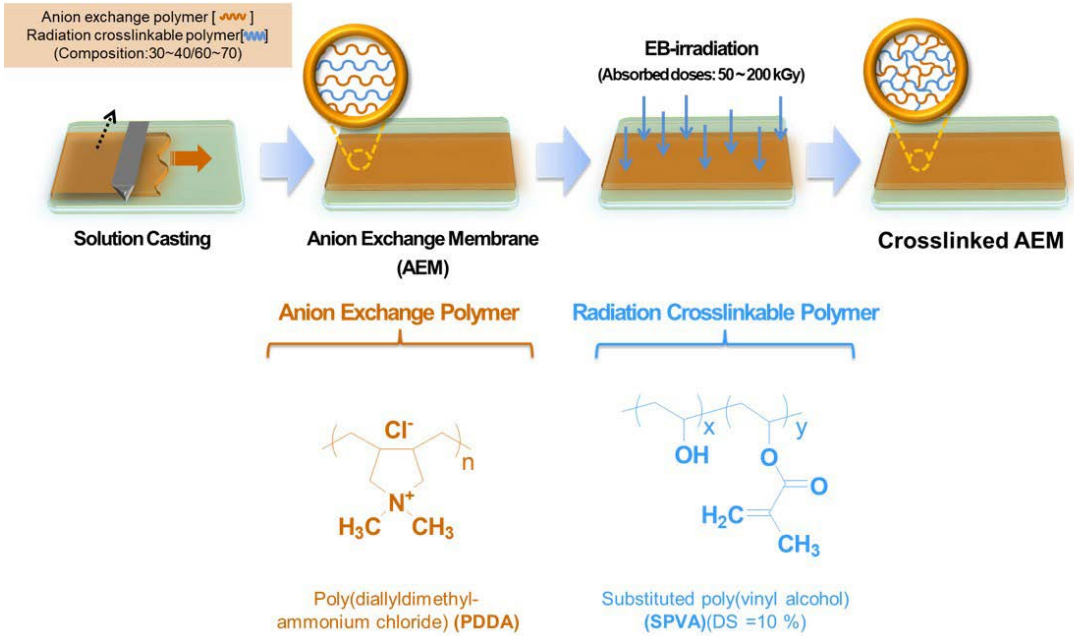


**Fig. 1.** Schematic procedure of the crosslinked PDDA/SPVA AEM by electron beam irradiation.

cluding operation at room temperature, solid-state chemical reaction without additives (initiator), higher throughput rates, and more precise control over the process. For these reasons, this technique has been widely used in the manufacturing of various industrial products including tire cord, heat-resistant electrical cable, polymer fuse, and polymer foam (Bhattacharya 2000; Clough 2001).

In previous study, we synthesized radiation-crosslinkable methacryloyl-substituted poly (vinyl alcohol) (SPVA) using a trans-esterfication of poly (vinyl alcohol) (PVA) with glycidyl methacrylate (GMA) and confirmed that SPVA was crosslinked by electron beam irradiation (Kim *et al*. 2019). Therefore, we propose an AEM based on SPVA and poly (diallyldimethylammonium chloride) (PDDA) with 100 mol% cyclic quaternary ammonium group in this study. The PDDA/SPVA AEMs with different composition were prepared by solution casting and underwent the exposure to electron beam irradiation at different doses. To investigate the radiation-crosslinking effect of PDDA/SPVA AEM, the crosslinked AEMs were characterized in terms of physicochemical, thermal properties.

## MATERIALS AND METHODS

### 1. Materials

Poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in $H_2O$, Mw 400,000~500,000) with 100 mol% ion exchangeable functional group (cyclic quaternary ammonium group), 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. Preparation of crosslinked AEM by electron beam irradiation

The preparation of crosslinked PDDA/SPVA AEMs via solution casting and subsequent electron beam irradiation were described as Fig. 1.

PDDA (poly(diallyldimethylammonium chloride), 20 wt% in $H_2O$) solution and 10 mol% methacryloyl-substituted PVA (SPVA) dissolved in DMSO (dimethyl sulfoxide) solvent were mixed to make a 10 wt% solution (the weight ratio of PDDA to SPVA was set to 40/60, 35/65, and 30/70) and then the solution casted on glass plates using a doctor blade. Afterwards, the resulting PDDA/SPVA membranes were dried in a vacuum oven for 6 h at 70°C to remove the remaining DMSO. For the electron beam irradiation, the prepared AEMs were put into aluminium pouches and thermally sealed after purging with $N_2$ gas. The sealed pouches were irradiated at room temperature with an ELV-8 electron beam

accelerator installed at EB-Tech (Daejeon, Korea). The energy and current density of the electron beam was 1.5 MeV and 7.2 $mA \cdot cm^{-2}$, respectively. The total absorbed dose and irradiation time were (50, 100, and 200) kGy and (90, 180, and 360) s, respectively.

### 3. Characterization

The gel fraction of the EB-irradiated AEMs was evaluated by measuring their insoluble part in the completely dried membranes after solvent extraction in DMSO at 50°C for 7 days. The gel fraction is calculated from the following equation:

$$Gel\ faction\ (\%) = W_d / W_i \times 100 \quad (1)$$

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

For determination of the water uptake, all samples were dried in a vacuum oven at 70°C for 1 day before the measurements. The samples were then immersed in de-ionized water for 7 days at 50°C to attain the equilibrium state. The water uptake value was calculated using the following equation:

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

where $W_s$ and $W_d$ are the weights of swollen and dried samples, respectively.

The ion exchange capacity (IEC) of the prepared membranes was measured using a titration method. Vacuum-dried membranes were immersed in 1 M NaCl solution for 1 day to fully attach chloride ions to positive charge area of membrane. Remnant NaCl was removed by deionized water. The sample was immersed in 2 M $NaNO_3$ for reaching equilibrium and then took out the sample. This solution was titrated against with 0.1 M $AgNO_3$ solution using $K_2CrO_4$ as an indicator (1 mL). Ion-exchange capacity was calculated as follows Equation (3):

$$IEC\ (meq \cdot g^{-1}) = \frac{V_{AgNO_3} \times C_{AgNO_3}}{W_d} \quad (3)$$

where $V_{AgNO_3}$, $C_{AgNO_3}$, and $W_d$ are volume and molar concentration of the titrated $AgNO_3$ solution, and dried samples, respectively.

Area resistance (R) of the AEM was determined according to the method proposed by Hwang and Ohya. The electric resistances of AEMs were measured in a two-compartment cell using a four-electrode configuration at room temperature. Two Ag/AgCl electrode were used as reference electrodes, while two platinum bars were used as working and counter electrodes. Two Luggin capillaries were used to minimize the distance (2 mm) between the reference electrodes. The resistances of two-compartment cell with membrane $R_1$ (Ω) and without membrane $R_2$ (Ω) were measured on AC impedance analyzer (SI1260, Solatron Company). Each compartment of the cell was filled with 0.5 M NaOH solution. S was the area of the prepared membrane ($cm^2$). R ($\Omega \cdot cm^2$) was calculated using the following formula:

$$R = (R_1 - R_2) \times S \quad (4)$$

Thermal analysis of the membranes before and after EB-irradiation was carried out using thermogravimetric analyzer (TGA, Q 500, TA Instrument). The analysis was conducted in the temperature range from 50°C to 800°C at a heating rate of $10°C \cdot min^{-1}$ under a nitrogen atmosphere.

Dimensional changes in the prepared AEMs were measured as a function of temperature by thermomechanical analyzer (TMA, Q400, TA Instrument) using extension probe between 50 and 300°C at a heating rate of $5°C \cdot min^{-1}$ under nitrogen atmosphere.

## RESULTS AND DISCUSSION

To observe SPVA as an efficient EB-crosslinkable polymer and absorbed dose effect on the formation of the crosslinked structure in PDDA/SPVA AEMs, the gel fraction of the control PDDA/PVA and PDDA/SPVA AEMs prepared at various composition and absorbed doses was investigated and the results are shown in Fig. 2. As shown in Fig. 2, the control PDDA/PVA AEM was completely dissolved within several hour while all EB-irradiated PDDA/SPVA AEMs at all composition reached the gel-fraction of 100% even at absorbed dose of 50 kGy. This result indicates that network structure is formed in PDDA AEMs by radiation-induced crosslinking with the crosslinkable polymer, SPVA (Woo *et al*. 2015; Kim *et al*. 2019).

The water uptake of the membranes is an important parameter to take into consideration for the determination of the physic-chemical property of AEMs. An excessive water swelling in the membrane induces the low dimensional stability and mechanical properties (Woo *et al*. 2015). Water

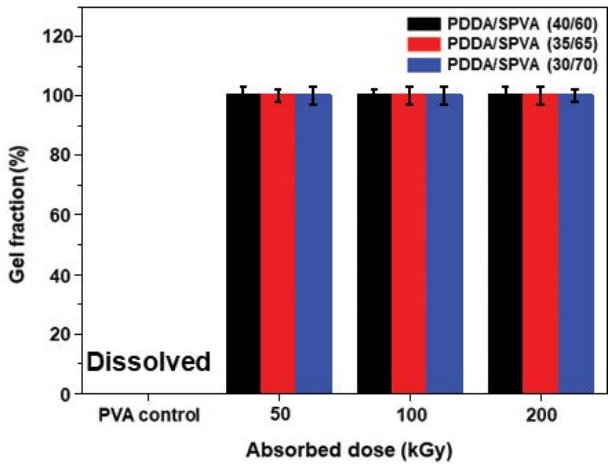


**Fig. 2.** Gel fraction of the EB-unirradiated PDDA/PVA (control) and the EB-irradiated PDDA/SPVA AEMs at the different doses.

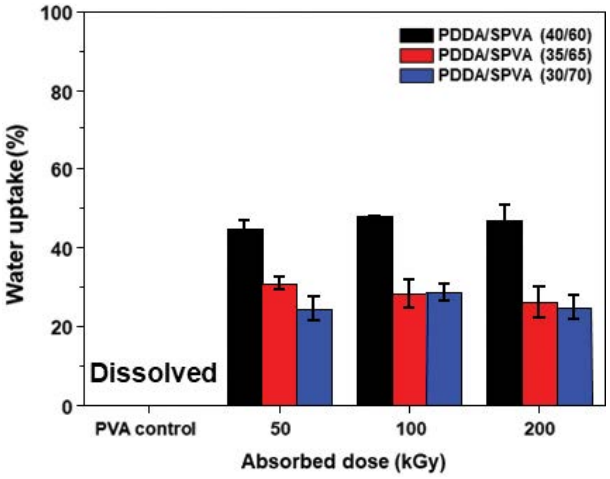


**Fig. 3.** Water uptake of EB-unirradiated PDDA/PVA (control) and the EB-irradiated PDDA/SPVA AEMs at the different doses.

uptakes of the control PDDA/PVA and PDDA/SPVA AEMs prepared at various composition and absorbed doses were measured at 50°C and the results are presented in Fig. 3. As shown in Fig. 3, we were not able to measure the water uptake of the control PDDA/PVA AEM because PDDA/PVA AEMs were dissolved in deionized water at 50°C within several hours. However, electron beam-irradiated PDDA/SPVA AEMs at all compositions were not dissolved in deionized water. In this figure, water uptake of electron beam-irradiated PDDA/SPVA AEMs at the absorbed dose of 50 kGy decreased with the increase in SPVA contents. However, at above 50 kGy, the irradiated membranes containing over 65 wt.% SPVA content exhibited the water uptake of below 30% and no significant change for the effect of electron beam on water uptake of the membranes at given conditions (above 50 kGy and 65 wt% SPVA contents). These results indicate that the electron beam irradiation at above 50 kGy and the presence of above 65 wt% SPVA as crosslinkable polymer are enough to improve the water uptake of the AEMs due to formation of crosslinking structure (Woo *et al*. 2015; Kim *et al*. 2019).

The ion exchange capacity (IEC), an indication of the total of the ion exchangeable groups (here, cyclic quaternary ammonium group) in the membrane, was measured using a titration method. Fig. 4 represented IEC values of the electron beam irradiated-AEMs with PDDA/SPVA composition of 35/65 and 30/70 at absorbed doses of 100 kGy and 200 kGy. As shown in Fig. 4, IEC of the membranes increased with the increase in PDDA content at all the given doses be-

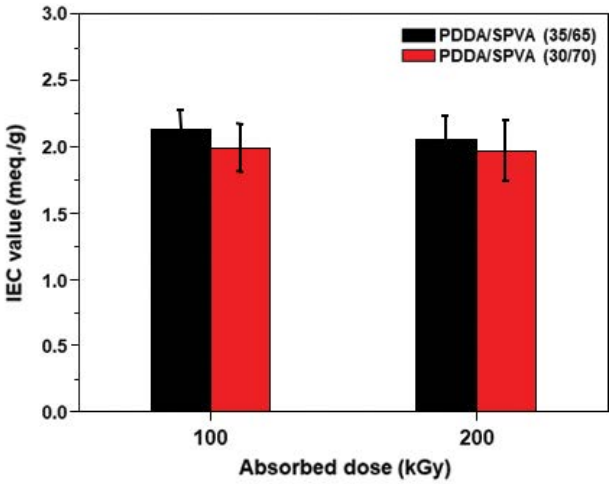


**Fig. 4.** IEC of the EB-irradiated AEMs with PDDA/SPVA composition of 35/65 and 30/70 at absorbed doses of 100 kGy and 200 kGy.

cause PDDA only contained ion exchangeable sites as cyclic quateranry ammomium group. However, it was found that no remarkably change of IEC in the membranes with same PDDA/SPVA composition through the electron beam irradiation doses changed from 100 kGy to 200 kGy. Therefore, these results reveals that cyclic quaternary ammonium groups in PDDA do not occur to degrade when electron beam is irradiated from 100 kGy to 200 kGy (Woo *et al*. 2015; Song *et al*. 2016). In this figure, it was confirmed that all the prepared AEMs showed high IEC of more than 1.7 $meq \cdot g^{-1}$.

In clean energy technology such as fuel cell, electrodialysis and capacitive deionization, membrane area resistance

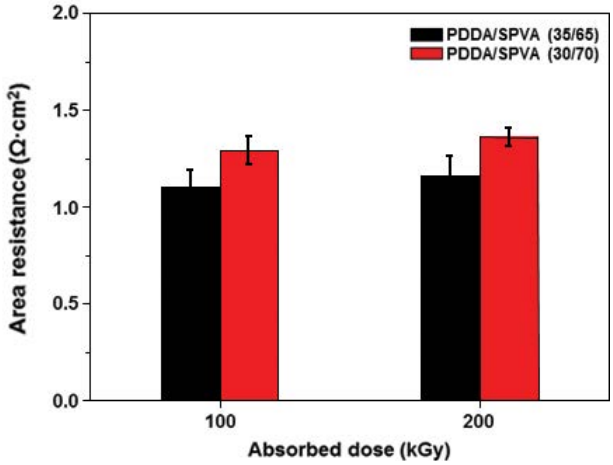


**Fig. 5.** Membrane area resistance of the EB-irradiated AEMs with PDDA/SPVA composition of 35/65 and 30/70 at absorbed doses of 100 kGy and 200 kGy.

of an AEM is one of important characteristics because mass transfer in AEM exploits a potential difference as the diving force (Khan *et al*. 2016). Fig. 5 shows the measurement results of the membrane area resistance of the prepared AEMs. In this figure, as the amount of SPVA, crosslinkable polymer, increased from 65% to 70%, membrane area resistance increased due to introduction of crosslinking structure and the decrease of ion exchange capacity (the decrease in the amount of PDDA) in the prepared membranes. However, it was found that there was almost no change of membrane area resistance in the membranes with same PDDA/SPVA composition even if the electron beam irradiation doses was changed from 100 kGy to 200 kGy (Song *et al*. 2016). In this figure, all the prepared membranes presented low membrane area resistances of below 1.4 $\Omega \cdot cm^2$.

Thermal stability of the EB-unirradiated control PDDA/PVA (35/65) and EB-irradiated PDDA/SPVA AEMs at 200 kGy were evaluated by TGA and TMA anaylsis in an $N_2$ atmosphere as in Fig. 6. As presented in Fig. 6(a), the TGA results showed EB-irradiated PDDA/SPVA (35/65) AEM had less weight loss compared to PDDA/PVA (35/65) one in the temperature range of 150 to 270°C and 300 to 400°C. These results indicate that the crosslinked structure was introduced into PDDA/SPVA (35/65) AEM by electron beam irradiation (Woo *et al*. 2015; Song *et al*. 2016). Also, as shown in Fig. 6(b), TMA results exhibited that the EB-unirradiated control PDDA/PVA (35/65) AEM was cut at 150°C, while the EB-irradiated PDDA/SPVA (35/65) AEM was thermally stable with only about 10% thermal shinkage. These results explain

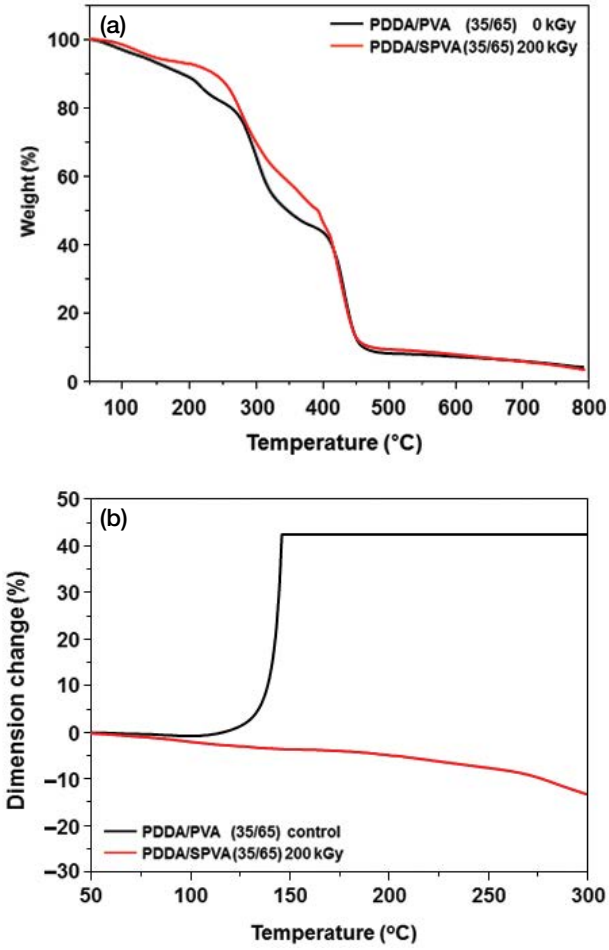


**Fig. 6.** TGA (a) and TMA (b) of the EB-unirradiated PDDA/PVA (35/65) (control) and PDDA/SPVA (35/65) AEMs at absorbed doses of 200 kGy.

that the crosslinked structure was effectively formed into the PDDA/SPVA AEM by the electron beam irradiation (Hwang *et al*. 2010; Choi *et al*. 2013).

## CONCLUSION

3D-network crosslinked AEMs with high IEC and superior water stability were fabricated by simple and quick radiation crosslinking technology using the mixture of anion exchange polymer (PDDA) with 100 mol% cyclic quaternary ammonium group and radiation-crosslinkable polymer (SPVA) in this study. It was confirmed from gel-fraction results that the crosslinked structure was successfully introduced in EB-irradiated PDDA/SPVA AEMs at all given PDDA/SPVA composition and absorbed doses. Also, we ascertained that EB-irradiated PDDA/SPVA AEMs with above 65 wt% SPVA content

at over 50 kGy absorbed doses exhibited the improved water uptake of below 30%, high IEC of above 1.7 meq·$g^{-1}$, and low membrane area resistance of below 1.4 Ω·$cm^2$ without degradation of ion exchangeable sites as cyclic quateranry ammomium group in PDDA by EB-irradiation. From TGA and TMA results, EB-irradiated PDDA/SPVA AEMs showed superior thermal stability compared to control PDDA/PVA AEMs. EB crosslinked PDDA/SPVA AEMs be useful in the development of alkaline fuel cells, electrodialysis, and seawater desalination application required of high IEC, water dimensional stability and thermal stability.

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