

Preparation and Characterization of Proton Conducting Membranes by Blending PVC-g-PHEA and PVA

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Abstract: This work reports the preparation of proton conductive crosslinked polymer electrolyte membranes by blending poly(vinyl chloride)-g-poly(hydroxyl ethyl acrylate) (PVC-g-PHEA) and poly(vinyl alcohol) (PVA). The PHEA chains of the graft copolymer were crosslinked with PVA using sulfosuccinic acid (SA) via the esterification reaction between -OH of polymer matrix and -COOH of SA. The PVC-g-PHEA graft copolymer was synthesized via atom transfer radical polymerization (ATRP) using direct initiation of the secondary chlorines of PVC backbones. Ion exchange capacity (IEC) continuously increased with increasing concentrations of SA, due to the increasing portion of charged groups in the membrane. However, the water uptake increased up to 20.0 wt% of SA concentration above which it decreased monotonically. The membrane exhibited a maximum proton conductivity of 0.026 S/cm at 20.0 wt% of SA concentration, which is presumably due to competitive effect between the increase of ionic sites and the crosslinking reaction.

Keywords: polymer electrolyte membrane, graft copolymer, poly(vinyl alcohol), crosslinking, proton conductivity

1. Introduction

Solid polymer electrolytes is a material which comprises metal salts dissolved in a polymeric matrix or the polymer backbones with covalently bonded ionizing groups attached to them. Polymer electrolytes have recently been of technological interest for the possible applications to energy conversion units such as batteries, fuel cells, solar cells, electrochromic display devices and facilitated transport membranes [1-4]. During the last decades, poly(vinyl chloride) (PVC) based polymer electrolytes have got their popularity in various applications due to their easy processibility, low cost and good compatibility with other components. However, only a few studies have been reported on the PVC based polymer electrolytes for proton conducting membranes.

During the past decades, sulfonated polymers have received much attention due to their significant technological use as ion-exchange resins, electrodialysis, bipolar membranes, sensors, and dehydration. Especially, sulfonated polymer membranes have been extensively investigated for the applications to fuel cells, as can be seen from the number of research papers [5-12]. The commercially available membranes in fuel cells are mostly based on perfluorosulfonic polymers such as Nafion, Gore-Select, Aciplex, Xus and Flemiom. They exhibited the excellent thermal and mechanical properties as well as high proton conductivity (around 0.1 S/cm at room temperature). However perfluorosulfonic polymers have some limitations such as high methanol permeability and high cost. Therefore, there has been a great deal of research into alternative sulfonated polymeric materials [13-21].

Here, a graft copolymer consisting of poly(vinyl chloride) (PVC) backbone and poly(hydroxyl ethyl acrylate)

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(PHEA) side chains was synthesized via atom transfer radical polymerization (ATRP). This graft copolymer was solution blended with poly(vinyl alcohol) (PVA) and thermally crosslinked with sulfosuccinic acid (SA), producing proton conducting crosslinked polymer electrolyte membranes. Several characteristics of the resultant polymer electrolyte membranes, e.g. ionic exchange capacity (IEC), water uptake and proton conductivity are reported in this paper.

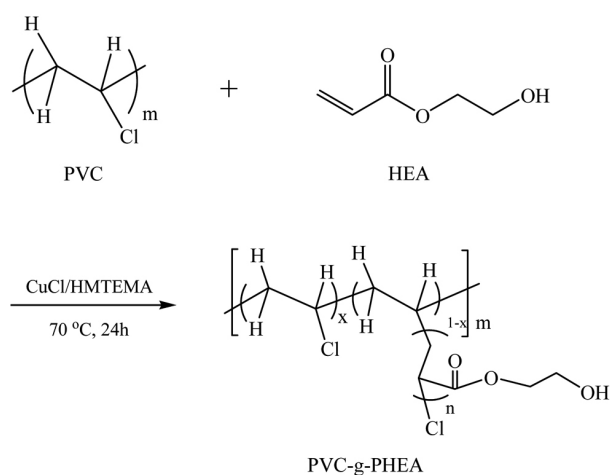
2. Experimental

2.1. Materials

PVC ($M_n = 55,000$ g/mol, $M_w = 97,000$ g/mol), 2-hydroxy ethyl acrylate (HEA, 99%), poly(vinyl alcohol) (PVA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%) and sulfosuccinic acid (70 wt% in water) were purchased from Aldrich. All solvents and chemicals were reagent grade, and used as received.

2.2. Synthesis of PVC-*g*-PHEA Graft Copolymer

Schematic procedure for the synthesis of PVC-*g*-PHEA graft copolymer is presented in Scheme 1. Two grams of PVC was dissolved in 18 mL of NMP in a round flask at 70°C. Then, 3.0 mL of HEA, 0.04 g of CuCl and 0.1 mL of HMTETA were added to the solution and the reaction flask was sealed with a rubber septum. After N₂ purging for 30 min, the reaction vessel was immersed in an oil bath at 70°C. The reaction was allowed to proceed for 24 h. After passing the solution through a column with activated Al₂O₃ to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. Finally, the polymer was dried in a vacuum oven overnight at room temperature. The product was gained as a form of powder and the grafting ratio was 15.0 wt%.



Scheme 1. ATRP for the synthesis of PVC-*g*-PHEA graft copolymer.

2.3. Preparation of Crosslinked PVC-*g*-PHEA/PVA Membranes

Different amounts of PVC-*g*-PHEA and PVA were dissolved in DMSO with stirring. After making homogeneous solution, the different amounts of SA were added into the polymer solution and stirred for more than 2 h. The polymer mixtures were then cast on a Teflon-coated glass dish, and dried in an oven at 80°C for two days. The obtained membranes were peeled off from the dishes and then annealed at 130°C for 3 h for crosslinking reaction. The membranes were washed with water several times to remove unreacted SA.

2.4. Ion Exchange Capacity (IEC)

IEC of the membranes was measured by the classical titration method. The membranes were soaked in 1.0 M NaCl solution for 24 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated against 0.01 M standardized NaOH solution, using phenolphthalein indicator. The experimental IEC of the membranes was calculated using the following equation.

$$\text{IEC (mEq/g)} = \frac{X \times N_{\text{NaOH}}}{\text{Weight (polymer)}} \quad (1)$$

where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

2.5. Water Uptake

Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent paper to remove the excess of water adhering to it and the sample was then weighed. The water uptake of the membrane was determined from

$$\text{water uptake (wt\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

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

2.6. Proton conductivity

A four-point probe method was used to measure the proton conductivity of the membranes using home made conductivity cell. Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range 1 Hz-8 MHz at 25°C, using a ZAHNER IM-6 impedance analyzer. The impedance spectra of the membranes can

be used to generate Nyquist plots, and the proton conductivity was calculated from the plots [21,22].

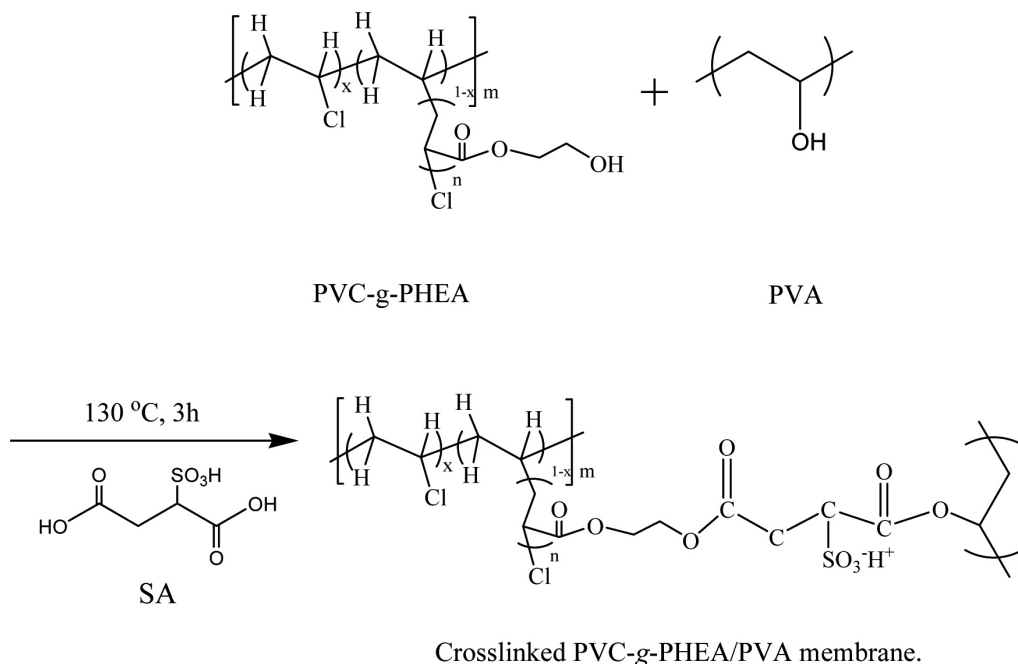
2.7. FT-IR Measurement

FT-IR spectra were recorded Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency range of 4000 to 400 cm^{-1} using ATR facility.

3. Results and Discussion

Scheme 1 shows the synthesis of PVC-g-PHEA graft copolymer. PVC backbone was directly grafted with HEA monomer at 70°C for 24 h through ATRP technique. The amphiphilic PVC graft copolymer is expected to molecularly self-assemble into continuous nanophase domains of semicrystalline PVC interweaved with hydrophilic domains of PHEA brush layer, providing a mechanism for facile proton transport through the membranes.

The synthetic procedure for crosslinked PVC-g-PHEA/PVA membranes is illustrated in Scheme 2. The as-synthesized PVC-g-PHEA graft copolymer was solution blended with PVA and thermally crosslinked with SA



Scheme 2. Schematic procedure for the preparation of crosslinked PVC-g-PHEA/PVA membranes.

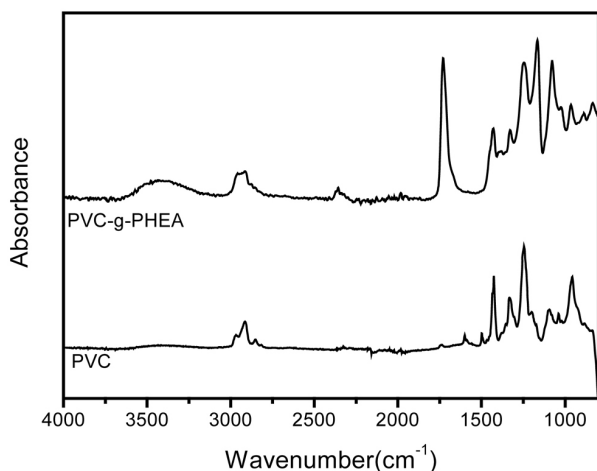


Fig. 1. FT-IR spectra of PVC, HEA and PVC-g-PHEA.

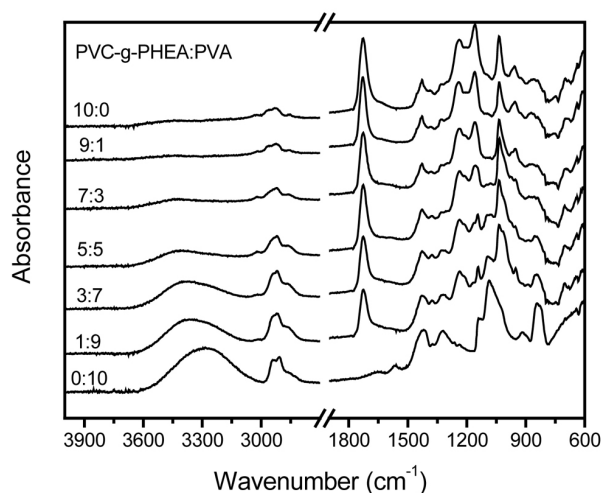


Fig. 2. FT-IR spectra of PVC-g-PHEA/PVA membrane before and after crosslinking.

at 130°C for 3 hours via the esterification between the -OH of PHEA/or PVA and the -COOH of SA. Because SA contains sulfonic acid groups, the crosslinked PVC-g-PHEA/PVA membranes possess proton conducting properties.

Fig. 1 shows the FT-IR spectra of pristine PVC and PVC-g-PHEA graft copolymer. The absorption bands at 1,728 and 1,167 cm^{-1} of PVC-g-PHEA graft copolymer are assigned to the carbonyl stretching vibration of PHEA, implying successful graft copolymerization from PVC. The broad band at 3,434 cm^{-1} is due to the hydroxyl group of PHEA in the graft copolymer.

Fig. 2 shows the FT-IR spectra of PVC-g-PHEA/

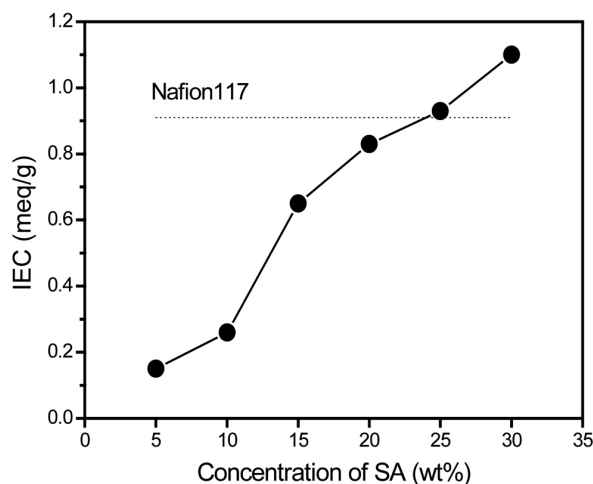


Fig. 3. IEC values of crosslinked PVC-g-PHEA/PVA membranes as a function of SA concentration.

PVA membranes with various ratios after crosslinking at 130°C for 3 h. Upon crosslinking of membranes, two stretching bands at 1,730 and 1,162 cm^{-1} grew up, attributable to the formation of -C=O and C-O in the membranes, respectively [23]. This result supports the crosslinking reaction of the membranes by the esterification between -OH of PHEA and -COOH of SA [24,25]. The shoulder peak at 1,230 cm^{-1} is due to the stretching vibration of the sulfonic acid groups of SA.

Fig. 3 shows the IEC values of crosslinked PVC-g-PHEA/PVA membranes as a function of SA concentration. The IEC values continuously increased with increasing amounts of SA, resulting from the increased portion of charged groups in the membrane. The membrane with 30 wt% of SA exhibited 1.1 meq/g of IEC value, which is higher than the IEC of Nafion 117. The high IEC value of the crosslinked PVC-g-PHEA/PVA membranes represent that the higher amounts of sulfonic acid groups are contained in the membranes.

Fig. 4 presents the water uptake of crosslinked PVC-g-PHEA/PVA membranes with the different amounts of SA. Upon the introduction of SA 5 wt%, the membrane exhibited 25% of water uptake. The water uptake of membranes gradually increased with SA concentration up to 20 wt% of SA concentration, after which they decreased monotonically. In general, water uptake is linearly proportional to the concentration of

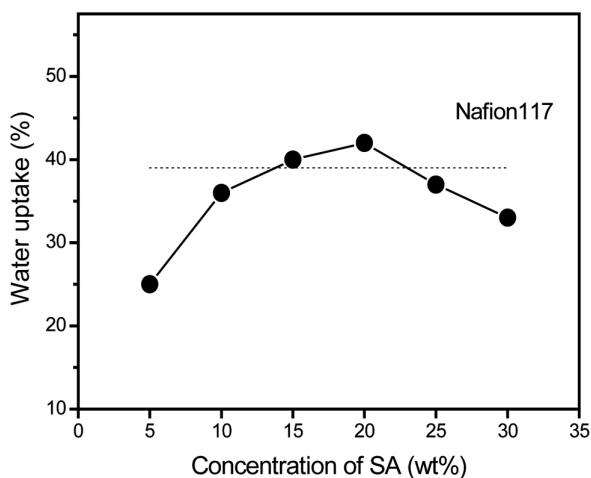


Fig. 4. Water uptake of crosslinked PVC-g-PHEA/PVA membranes as a function of SA concentration.

ionic SO_3^- groups, i.e. IEC value. In this work, however, the water uptake was not increased linearly with SA content, which was not consistent with the behavior of IEC values shown in Fig. 3. It may be explained by the fact that the introduction of SA produces crosslinking of the membranes, resulting in more rigid and compact structures of membranes. Thus, water uptake of membranes was decreased to some degree at higher content of SA.

The proton conductivities of crosslinked PVC-g-PHEA/PVA membranes at room temperature are presented in Fig. 5 as a function of the concentration of SA. As shown, proton conductivities were significantly dependent upon the SA concentration, i.e. the contents of acidic SO_3^- groups and the degree of crosslinking. The proton conductivity of membranes was initially increased with SA concentration up to 20 wt%, after which it is gradually decreased. This behavior is attributable to the competitive effect between the increase of ionic sites and the crosslinking reaction, according to the SA concentration. Overall, the proton conductivities of crosslinked PVC-g-PHEA/PVA membranes were in the order of $10^{-3} \sim 10^{-2}$ S/cm at room temperature. A maximum proton conductivity of 0.026 S/cm was achieved at 20.0 wt% of SA concentration.

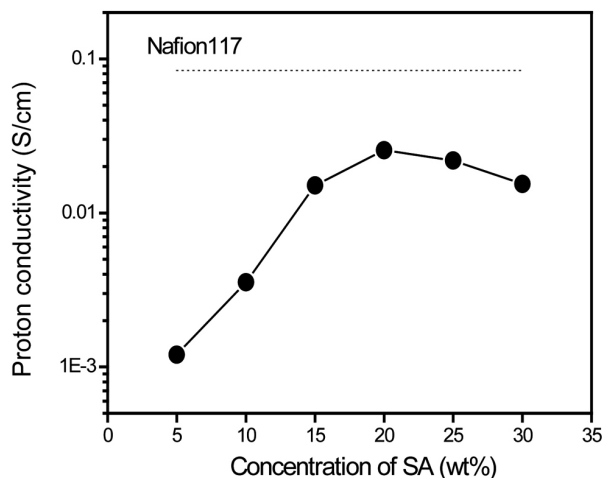


Fig. 5. Proton conductivity of crosslinked PVC-g-PHEA/PVA membranes as a function of SA concentration.

4. Conclusion

PVC-g-PHEA graft copolymer was synthesized via ATRP process using PVC backbone as a macroinitiator. The proton conducting crosslinked membranes were developed by blending the PVC-g-PHEA graft copolymer and PVA, followed by thermal crosslinking reaction with SA. The IEC values continuously increased with increasing SA concentrations whereas the water uptake increased up to 20.0 wt% of SA concentration above which it decreased monotonically. In accord with water uptake, the proton conductivity of crosslinked PVC-g-PHEA/PVA membranes at room temperature increased up to 20.0 wt% of SA concentration, above which it decreased. A maximum proton conductivity of crosslinked PVC-g-PHEA/PVA membranes was achieved as 0.026 S/cm at 20.0 wt% of SA concentration. This maximum behavior was elucidated in terms of competitive effect between the increase of ionic sites and the crosslinking reaction with increasing SA concentrations.

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