PVA/PAM 막의 aging effect

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Aging effect of poly(vinyl alcohol) membranes with poly(acrylic acid-co-maleic acid)

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1. Introduction

In our previous study, the crosslinked PVA/PAM membrane was prepared to investigate the pervaporation performance, and analyzed by FT-IR and water swelling test. This main objective of this work was to investigate the aging effect of PVA/PAM membrane with swelling time. To do this, the introduction of carboxylic group into PVA matrix was achieved by the modification of PVA chemical structure through esterification with PAM containing carboxylic group, the PAM was used as a crosslinking agent and as a donor of the hydrophilic COOH group. Here, we expect that the introduction of carboxylic acid group in the polymer chain makes to be facilitating the conduction of proton. The structure of the membrane with swelling time is characterized by AFM, the water state and the performance of the membranes is determined by proton conductivity.

2. Experiment

The crosslinked PVA/PAM membranes were prepared with the following two steps. First, Aqueous 10 wt.% PVA solutions were prepared by dissolving pre-weighed quantities of dry PVA in water and then refluxing at 90℃ for 6h and aqueous PAM was dissolved in water at room temperature. Then PVA solutions were mixed together along with PAM solution until forming a homogeneous solution for 1 day at room temperature. The membranes were immersed in water at 100℃ from 1day to 7days.

Differential scanning calorimeter (DSC) measurement was carried out using a DSC 2010 thermal analyzer (TA Instrument, NewCastle, DE, USA) equipped with a cooling apparatus. Atomic force microscopy (AFM) imagines were performed in air using a Digital Instruments Nanoscope II.

Weight change ration of the membranes studies were carried out to investigate the aging effect of the membranes. The ion exchange capacity(also known as IEC value) was measued using the classical titration. The Proton conductivity of membranes was measured using the normal four-point probe techique at RH 95%.

3. Results and Discussion

As shown in Figure 1 (a), the weight change ratio of the membrane increased with the swelling time. The 30 wt.% weight loss of the dry membrane was observed in the swelling test for 6 days. However, the total water content increases with swelling time as shown in Figure 1 (b). This result suggested that the unreacted monomer was released from the membrane with swelling time, and the ester bond between OH and COOH was partially decomposed at experimental condition such as boiling water swelling test. This behavior was confirmed with the state of water using DSC experiment, and IEC value. The prepared proton exchange membranes at each swelling test condition possessed IEC values in the range of 0.85 ~ 1.59 meq/g-dry membrane.

Generally, the proton conductivity is dependent on the state of hydration of the membrane. In a water swollen membrane, the protons are solvated and enabled to be transported through the membrane. The proton conductivity of the membranes measured at T = 30, and 50℃ was in the range of 10^{-3} ~ 10^{-2} S/cm, and slightly increased with swelling time, and temperature. This behavior was attributed to increase the ionic site due to decomposing ester bond, and hydration state.

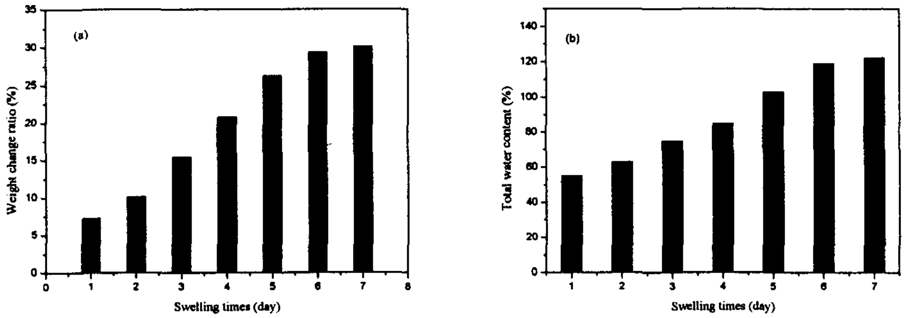

Fig. 1 (a) weight change ratio, (b) total water content of the membranes with swelling time

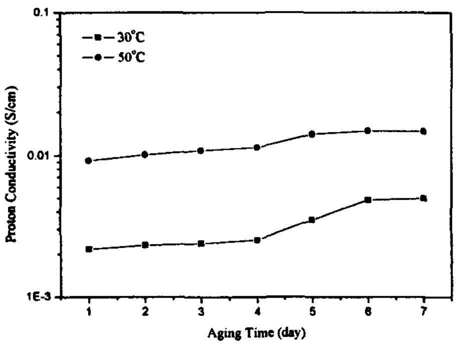

Fig. 2 Proton conductivity of the PVA/PAM membranes at RH 95%

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