P-15

Effect of Annealing and Polymeric Additives on Permeation Properties of Asymmetric Polyacrylonitrile Membranes

Joon Ki Yoon, Bumsuk Jung*, Hee Woo Rhee, Yong Soo Kang*

Sogang University, *KIST

(bjung@kist.re.kr)

1.Introduction

Since Loeb and Souriajan first introduced phase inversion method [1], much investigation has been made for understanding the mechanism of formation of asymmetric membranes. Phase inversion is the most extensively used technique for the preparation of asymmetric membranes, which is that cast solution film on a substrate is immersed and is precipitated in water bath. It usually turns out to be a characteristic morphology of asymmetric membrane showing a dense top layer and porous sub layer [2]. When asymmetric membranes are prepared using polymer solutions composed of the PAN and PVP and solvent, DMSO through classical phase inversion method. By adding the different molecular weight of PVP to the solutions, the effect of molecular weight of PVP on morphological and transport properties of the asymmetric membranes such as water flux and rejections will be discussed. Lastly, it will be investigated how the characteristics of water permeation changes when the residual PVP is selectively composed through the hypochlorite treatment.

The effect of annealing in hot water on the basic properties of blend films of PAN/PVP was first investigated, compared to PAN film. Next, the crystallization, morphological and transport properties of the asymmetric polyacrylonitrile membranes were investigated, related to the annealing conditions.

2. Experimental

2.1. Preparation and filtration of asymmetric membrane

The membrane was prepared from 12wt% of PAN solutions with three different molecular weight of PVP (10K, 46K, 360K). The membranes were cut into disks with diameter of 43 mm for setup in a filtration cell (Amicon Co. Ltd. Type 8050).Pure water flux experiments were performed by applying pressure from 0.5 to 2 kg/cm^2.

Rejection was determined by a standard dextran (Mw = 160K, Sigma). Using low concentration feed of dextran (0.5wt%), the solute rejection experiments were performed under a low pressure of 0.5 kg/cm^2.

2.1. Scanning Electron Microscope and FT-IR

The morphology of membranes was observed with Scanning Electron Microscope (S-2500C, NORAN INSTRUMENTS, INC., USA). Samples were freeze-dried under vacuum before fracturing under cryogentic condition using nitrogen. Quantitative analysis of PAN and PVP were performed by FT-IR (DruSampl-IR-II, SensIR Technologies).

2.2. Hypochlorite treatment of membranes

5,000 ppm of aqueous NaOCl solution was prepared in 100 ml beaker. The membranes were immersed in the NaOCl solution for 2 hours and then were placed in deionized distilled water for 5 hours.

2.3 Wide Angle X-ray Scattering (WAXS)

X-ray diffraction patterns of PAN film samples were obtained using a MAC SCIENCE X-ray generator at 40kV of the acceleration voltage with 40mA of supplying current. The scattered X-ray in WAXD mode was monochromatized to CuKα (1.54 Å) with a graphite monochromator, and counted with a MAC SCIENCE scintillation counter at intervals of 0.02°scattering angle using a MXP 18A-HF goniometer.

3. Result and discussion

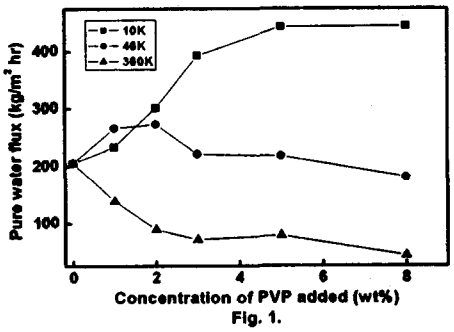

Fig. 1.

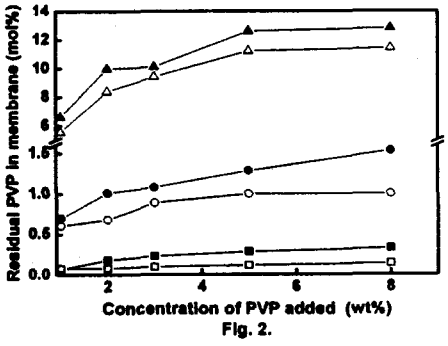

Fig. 2.

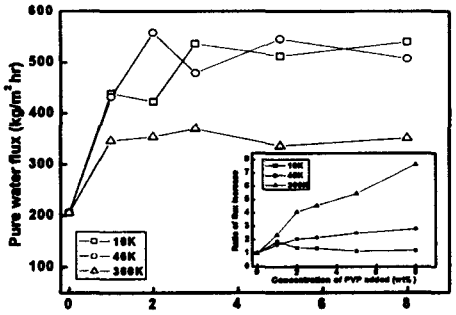

Fig. 3.

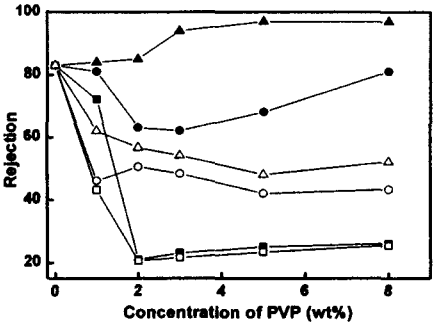

Fig. 4.

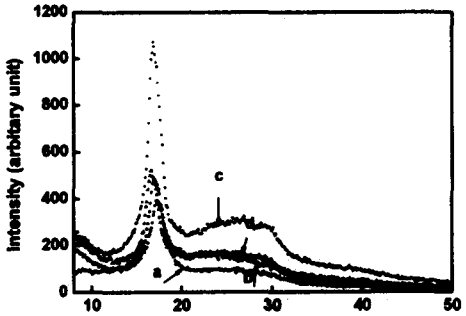

Fig. 5.

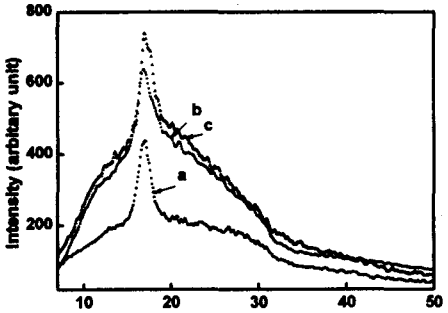

Fig. 6.

3.1. The effect of molecular weight of PVP on water flux

It is important to see how the thicknesses of top layers have an effect on the permeation, the water fluxes of the membranes are measured. Figure 1 shows the water flux changes with concentration of additive, PVP. The pure water flux of the membrane made by 12 wt% of the additive-free PAN solution exhibits 205 LMH whereas the flux of the membrane prepared with 12of PAN solutions with three different molecular weight of PVP (10K, 46K, and 360K) show different permeation fluxes.

3.2. Characterization of residual PVP after hypochlorite treatment

As shown in Fig. 2, the residual amount of PVP increase as the addition of PVP increase, and as the higher molecular weight of PVP are added the more amount of PVP are resided.

3.3.Effect of the hypochlorite treatments on permeation property and morphology

To investigate the effect of the hypochlorite treatment on water flux, water permeation test was performed. Fig. 3 shows the pure water flux changes after the hypochlorite treatment, and the amount of flux enhancement is also illustrated in the

inset plot as a function of PVP added. As can be seen in Fig. 3, the water flux by the hypochlorite treatment is quite noticeable.

After the hypochlorite treatment, the rejection of low molecular weight of PVP (10K) is not varied, but the rejection of the rest of two systems (46K, 360K) decreases. It seems that the hypochlorite process affects the size and numbers of pores although PVP is partially decomposed.

3.4. Crystalline structure of PAN and PVP blend films by water

Although it has been argued about the crystal structure of PAN, it is usually shown that a sharp diffraction is observed at $2\theta = 17^{\circ}$ (d=5.3 Å), and amorphous halo also exhibits between $2\theta = 20 \sim 30^{\circ}$ and relatively weak diffraction is found at $2\theta = 30^{\circ}$ (d= 3 Å) [3]. The crystallographic studies haverevealed that PAN is composed of hexagonal packing of rod-like chain [4] and the degree of crystalline is known as about 40%, which is also dependent on the preparation condition [5]. As can be seen in Figure 4, the as-prepared film of PAN shows a distinct crystalline peak is observed at $2\theta = 17^{\circ}$ (Fig. 5(a)). The degree of crystallization was estimated as 0.45 and their apparent crystallite size (t) was 49.95 Å by Bell and Dumbleton method [3, 6].

It might be very interesting how a fraction of PVP in PAN films affect the crystallization and the size of crystal, because a top layer in the asymmetric membrane became denser when PVP is blended after hot water annealing. As well-known that PAN is quite miscible with PVP for all composition [7].

4. Conculsion

The water flux depends on the structure of membrane as well as on the pore-filled PVP. It wasalso found that as the higher molecular weight of PVP and the more amount of PVP were added, the more amount of PVP were remained. After hypochlorite treatment, the selective removal of residual PVP in the PAN membranes was more effective, when higher molecular weight of PVP was filled in pores. It should be noted that due the water flux was enhanced, to the effective removal of PVP without changing the micropores. Due to the decomposition of PVP by NaOCl, the surface membranes are smoother.

It was found that PVP, which is miscible with PAN, is quite effective to control the morphologyof PAN membranes by adding it to casting solutions. More than 50% of PVP was dissolved out while the membranes were fabricated through phase inversion process. As more PVP was added to polymer solution, aso-called skin (top) layer is thicker and the micropores in the top layer are more porous. Due to the entrappedPVP,

the pure water flux declines as the concentration of PVP in the casting solution increases. When as-prepared membranes were annealed in hot water (80°C), the sizes of micropores were reduced and much of residual PVP in the as-prepared membrane were washed out. The amount of PVP washed by annealing was noticeable as smaller amount of PVP were resided.

5. Reference

[1] G.S. Loeb, S. Sourirajan,Sea water demineralization by means of an osmotic membrane, Advances in Chemistry Series, ACS, 38 (1963) 117.

[2] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht, 1991.

[3] A.K. Gupta, R.P. Singhal, Effect of copolymerization and heat treatment on the structure and X-ray diffraction of polyacrylonitrile, J. Polym. Sci.; Polym. Phys. Ed., 21 (1983) 2243.

[4] Z. Bashir, Thermoreversible gelation and plasticization of polyacrylonitrile, Polymer, 33 (1992) 4304.

[5]A.K. Gupta, N. Chand, Effect of copolymerization on the crystalline structure of polyacrylonitrile, Eur. Polym. J., 15 (1979) 899.

[6] J.P. Bell, J.H. Dumbleton, Changes in the structure of wet-spun acrylic fibers during processing, Text. Res. J., 41(1971) 196.