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Effect of crystallization and annealing on polyacrylonitrile membranes for ultrafiltration

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Abstract

Polyacrylonitrile (PAN) membrane is known as one of the hydrophilic membranes for ultrafiltration. However, the membrane has been preventing from the versatile applications, because the semi-crystalline PAN membranes are so brittle that cannot reuse once the membrane has been dried. The effect of crystalline domains in asymmetric polyacrylonitrile membranes is investigated, when the membranes are annealed in hot water and when the membranes are dried. Asymmetric polyacrylonitrile membranes were prepared via phase inversion process in a water bath and the effect of additive, PVP to the casting solution on the morphology and the water flux and the rejection were investigated. When the membranes were annealed in hot water (80 °C), the size of pores have been reduced and the water flux also decreased. Using wide angle X-ray scattering (WAXS), the effect of absorbed water on PAN membranes was studied. The absorption of water in PAN membranes mainly occurred through amorphous phase like a plasticizer, and induced the change of crystalline structure. The size of crystallite and the degree of crystallinity have changed when the membrane were annealed in the hot water. When the asymmetric PAN membranes were dried, the moisture also plays a crucial role in transforming the crystalline structures. The kinetics of drying strongly influences the size of crystallite as well as the crystallinity.

Keywords: Ultrafiltration; Additive; Crystallization; Morphology; Membrane characterization

1. Introduction

Polyacrylonitrile (PAN) is one of the fascinating membrane materials, because it is so hydrophilic that has been commercialized for ultrafiltration and microfiltration [1]. Compared to other membrane materials such as polysulfone (PSf), polyethersulfone (PES), polyethylene (PE), and polypropylene (PP), the unique hydrophilic property of PAN membrane shows a low fouling effect on the membrane process for water treatment. Nevertheless, PAN membrane causes a serious problem in the practical use of filtration process. When the films and membranes of microporous PAN were allowed to be dried, it became so brittle that could not be bent even without snapping. In fact, it has been reported that the role of moisture entrapped in PAN materials is a plasticizer, which is confirmed through IR and Raman spectroscopic experiments, since the morphological change of crystal was observed from hexagonal to orthorhombic polymorph through WAXS experiments [2].

PAN is one of the semi-crystalline polymers and the physical and mechanical properties strongly depend on the crystalline structures. The unit cells and the crystalline structures of PAN are still under debates, because the thermal history of PAN exhibits different polymorph. Nevertheless, there are two types of unit cells have been proposed, i.e.

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hexagonal or orthorhombic, which is depends on whether the unit cells with a repeating unit along the chain axis have. Despite the debate, WAXS result for the fully dried powder of PAN exhibits the two identifying peaks with *d*-spacing of 5.30×10^{-10} and 3.05×10^{-10} m [3–5]. According to Bashir [6], when the hexagonal polymorph of PAN films were plasticized by a small fraction of water at high temperature, the five peaks (*d*-spacing = 10.10×10^{-10}, 5.31×10^{-10}, 5.11×10^{-10}, 3.33×10^{-10}, 3.05×10^{-10} m) were observed from WAXS, and the hydrated orthorhombic polymorph was also found when the hydrogen bond between the hydrated water and the nitrile group exists.

PVP, which is known as a nontoxic material widely used for biomedical applications, is one of good polymer additives as a pore forming agent, because PVP is miscible with many of membrane materials and is quite well soluble in water as well as in solvents. It has been known that PVP is well miscible with PAN. According to Guo et al. [7], the blends of PAN/PVP are compatible over all compositions, and show single glass transition temperatures. In fact, it has been widely studied that the effect of PVP addition as a pore-forming agent to the casting polymer solutions on the formation of phase inversion membrane [8]. Since the high molecular weight of PVP is likely to entrap in the membranes during the fabrication of asymmetric membrane, the resulting membranes turn out to be more hydrophilic, and the macrovoid formation disappears as more PVP is added to the casting solutions [9].

Nouzaki et al. [10] reported that the water flux decreased and the rejection increased as the prepared PAN membranes were annealed in water at 60 °C and the mechanical property of the membrane was also enhanced. In addition, it has been similarly reported that when PAN membranes were annealed in a water bath (90 °C) for 10 min, the water permeability decreased, but the pore size of surface was not changed. However, the roughness of top surface decreased due to a melting-down of top surface by Paul et al. [11]. Despite of interesting results, it is not clear how the annealing process in hot water influences on the membrane performance. Thus, it is necessary to know how the uptake of water in the PAN membrane affects microstructure, and is important to obtain the information on the molecular structure for the annealing and the drying process, while a small fraction of additive, PVP is entrapped.

In this report, the asymmetric PAN membranes were prepared via phase inversion process from the casting solutions composed with PAN, PVP and DMSO. The change of membrane characteristics will be investigated when the prepared membranes are annealed in hot water, and then the effect of annealing in hot water on the basic properties of blend films of PAN/PVP are investigated, compared to the form of PAN films. Next, the crystallization, morphological and transport properties of the membranes will be investigated, related to the annealing conditions. Finally, the change of crystallization will also be studied while the membranes are dried, in order to elucidate the kinetics of crystallite formation in PAN membranes by removing the uptake water.

2. Experimental

2.1. Materials

PAN (MW; 150,000) was obtained from Aldrich and PVP (K-80, MW; 900,000) was obtained from BASF. The solvent, dimethylsulfoxide (DMSO) from Aldrich was used without purification. Deionized water purified with Milli Q system (Millipore) was used throughout experiment.

2.2. Preparation and annealing of asymmetric membrane and water permeability

The asymmetric membranes were prepared by phase inversion method using water as a coagulant. The two polymers of PAN and PVP with different compositions were dissolved in DMSO to be 12 wt% PAN concentration. The dope solutions were poured onto a glass plate, and were cast to be 200 μm thick with a doctor's blade. The glass plate was immediately immersed in a water bath at room temperature. Thus, the obtained membranes were kept in the water bath for 24 h to be fully coagulated, and then the membrane was washed with deionized water before filtration experiment. The annealing of the membranes was performed by immersing the membranes in 80 °C water bath for 24 h before further experiments. The membranes for filtration test 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 the transmembrane pressure from 0.1 to 2 kg/cm^2. Solute rejections experiments were performed using PEG (Mw = 20K, Mn/Mw = 1.08, polymer source, Canada). Using the low concentration feed of PEG (0.5 wt%), the solute rejection experiments were performed under a low pressure of 0.5 kg/cm^2. The permeated samples were collected for 1 min and the concentrations of permeate were determined by differential refractive index detector (RI 750F, Younglin, Korea).

2.3. Scanning electron microscope and infrared spectroscopy

The morphology of membranes was observed with scanning electron microscope (S-2500C, Noran Instruments). Samples were freeze-dried under vacuum before fracturing using liquid nitrogen. The quantitative analysis of PAN and PVP were performed by FT-IR (DruSampl-IR-II, SensIR Tech.). The quantitative calibration of PVP and PAN was carried out, using PAN/PVP blend films prepared with different compositions, because each functional group has different oscillation strength. By evaluating the peak areas of carbonyl (–CO) and nitrile (–CN) groups in blend films, a master curve