포스터 발표 P-19

고투과성 폴리벤즈옥사졸-실리카 복합막의 기체투과특성

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Gas Permeation Characteristics of High Permeable Polybenzoxazole-silica Hybrid Membrane

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1. Introduction

In gas and vapor separation field, high free volume glassy polymers such as PTMSP[1], PMP[2], AF2400[3] have been concerned because of their unique gas transport properties. These polymers have high fractional free volume and high gas and vapor permeability in spite of glassy polymers due to their inter-connected microporous structure. However, they have lower gas selectivities with physical aging problem. To overcome these glassy polymer membrane's weak point, high permeable aromatic polybenzoxazole was fabricated from in-situ thermal conversion of hydroxy-containing polyimide[4]. During the conversion process, 2 moles of CO_2 was evolved from the polymer matrix and this procedure gives high gas permeability with good selectivity. Here we improved their gas permeation properties by dispersing the nano-sized fumed silica in polymer matrix with adequate dispersing agent. In this study, polybenzoxazole-silica composite membranes were prepared to improve their gas permeation properties with good thermal, mechanical properties. the dispersing agent and solvent effect was analyzed with various silica content and character.

2. Experimental

2.1. Preparation of polybenzoxazole(PBO) precursor containing hydrophilic and hydrophobic fumed silica

In order to synthesize the precursor, functionalized polyimides, we performed typical two-step thermal imidization method. 4,4′ - (hexafluoroisoproypylidene) - diphthalic anhydride (6FDA) and hydroxy group containing 2,2′ - bis(3 - amino - 4 - hydroxy - phenyl)hexafluoropropane (APAF) were used to render hydroxy containing poly (amic acid). Before the thermal imidization process, 1 wt% of hydrophilic (aerosol 200, Degussa, BET surface area = 200 m^2/g) and hydrophobic (aerosol 812, Degussa, BET surface area = 260 m^2/g) fumed silica was introduced with dispersing agent (PEG, Mw = 10000, 20000, 35000) in N-methylpyrrolidone or CCl_4. Polymer solution was prepared in a high speed mixer during 60 min at 1200 rpm to obtain homogeneous particle dispersion. After thermal imidization step, silica dispersed hydroxy containing polyimide films were prepared. Also these films were thermally treated in the appropriate temperature range (400~500 °C) in order to prepare nano-composite PBO membranes.

2.2. Characterization of silica-PBO composite membranes

Thermally converted silica-PBO composite membranes were characterized by using the FT-IR spectroscopy, thermo-gravimetric analysis, X-ray diffraction pattern, BET adsoprtion measurement, SEM images. Finally, Gas permeation experiment was performed to characterize silica-PBO composite membranes.

3. Results and discussion

Single gas permeation data for He, H_2, CO_2, O_2, N_2 and CH_4 were determined by the time-lag method at 25 °C, 760 torr feed pressure. Fig 1. shows the gas permeabilities of 6F-PBO, 1 wt% silica-containing PBO with different kinds of PEG (Mw = 10,000, 20,000, 35,000) as dispersing agent. Generally, Incorporation of silica gives rise to high gas permeability to all kinds of gases.

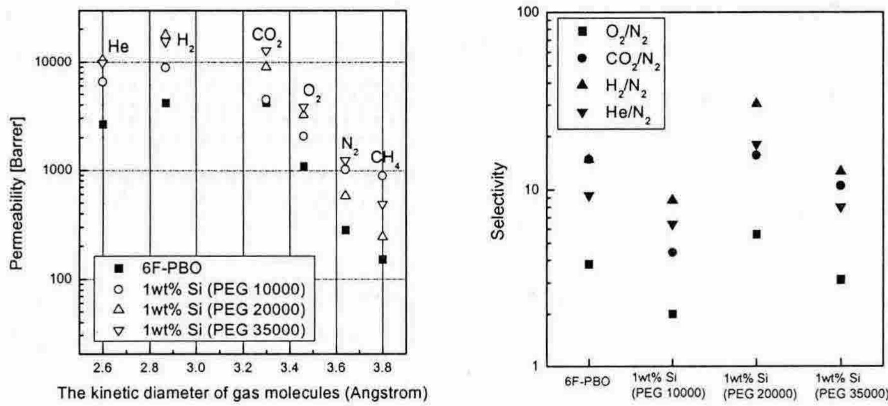

Fig 1. Gas permeabilities and selectivities of silica-PBO composite membranes

The effect about molecular weight of dispersing agent was not huge but 1wt% Si (PEG 20000) was most permeable and selectable for small permanent gases such as He, H_2.

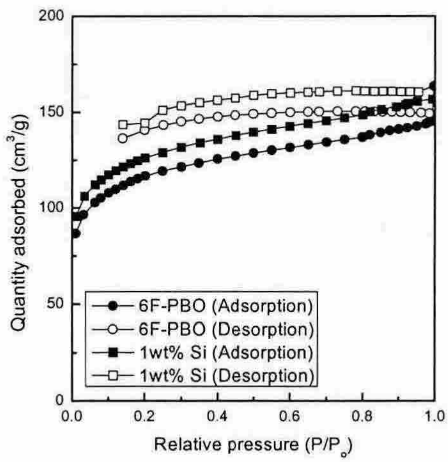

Fig 2. N_2 adsoprtion and desorption isotherm of 6F-PBO and 1wt% Si (PEG 10000)

N_2 adsorption and desorption isotherms measurements were carried out in order to compare the pore size, pore volume and surface area. Fig 2 shows the isotherm linear plot for 6F-PBO and 1wt % Si samples. N_2 gas was more adsorbed to 1wt % Si than pure 6F-PBO which caused by the incorporation of silica having high surface area (200 m^2/g).

4. Conclusions

Silica-PBO nano composite membranes were easily prepared with suitable dispersing agent. Obtained films showed much higher mechanical and thermal stability than pure PBO films. Gas permeation characteristics of silica composite membranes were intended to increase their flux with no loss of selectivity.

Reference

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