

신규 폴리벤즈옥사졸-폴리피롤론 공중합막의 합성 및 기체 투과 특성 고찰

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Synthesis and gas permeation properties of new polybenzoxazole-polypyrrolone(PBO-PP) copolymer membranes

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1. Introduction

To enhance the gas permeability and selective properties of conventional polymeric membranes, many researchers have tried to modify polymeric materials with various method [1,2,3]. For polymeric membrane separation process, the main disadvantage is the poor performance to separate gases or liquids with physical aging problem or inherent demerit. Here, we have surveyed manifold candidate polymeric materials and preparation method. Here, we have found the possible formation of gas-accessible micropores (microvoids or free volume) from chain disruption or molecular rearrangement in a solid state (power or film) of glassy polymers with chain packing calibrated to generate organic molecular sieves. We have focused on to the *in-situ* thermal conversion of some functionalized polyimides (e.g., hydroxy-containing polyimides) into high performance polymers (e.g., polybenzoxazoles)[4], possessing excellent mechanical, thermal and chemical stability in a condensed solid state. For this reason, we prepared polybenzoxazole-polypyrrolone (PBO-PP) block/random (b/r) copolymer and researched their O₂, N₂ permeability and their selectivity (O₂/N₂).

2. Experimental

In order to synthesize the precursor, functionalized polyimides, of r/b PBO-PP copolymer, we performed typical two-step thermal imidization method. 4,4' - (hexafluoroisopropylidene) - diphthalic anhydride (6FDA) was used for anhydride portion. hydroxy group containing 2,2' - bis(3 - amino - 4 - hydroxy - phenyl)hexafluoropropane (APAF) and 3,3' - diaminobenzidine was prepared to give functionality to the polyimide backbone. After the functionalized (hydroxy-, amine- group containing) co-polyimide was synthesized, thermal treatment was carried out to make PBO-PP membranes. Thermal treatment was carried out at 450 °C for 1 hour in an inert atmosphere. Finally, hydroxy- and amine-containing polyimides were converted to polybenzoxazole and polypyrrolone respectively. The thermal conversion was examined by FT-IR, TGA thermogram, X-ray diffraction, BET adsorption experiment. Also we performed single gas permeation experiment for O₂, N₂ in order to confirm the effect of thermal rearrangement of functional groups and the difference of preparation method, random, block copolymerization.

3. Results and discussion

Fig 1. shows the thermogravimetric analysis curves and mass spectroscopy of r/b-PBO-PP copolymer.

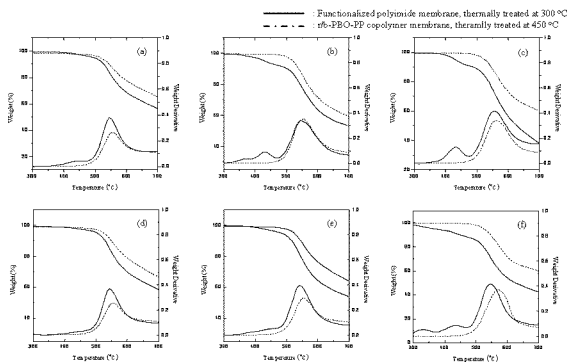


Fig 1. TGA thermogram of PBO-PP copolymer membrane according to their chemical composition: (a) b-PBO-PP(2:8), (b) b-PBO-PP(5:5), (c) b-PBO-PP(8:2), (d) r-PBO-PP(2:8), (e) r-PBO-PP(5:5), (f) r-PBO-PP(8:2)

In the case of functionalized polyimides, the first weight loss was observed between 350–450 °C. However the thermally treated r/b-PBO-PP membrane shows no weight loss at the temperature region. Also we observed the increase of weight loss as the amount of PBO segment in polymer main chain increases. It was concluded that PBO segment may produce more thermal rearrangement site than PP. The second weight loss began at about 500 °C because of main chain breakage. Single gas experiment was performed by using time-lag method.

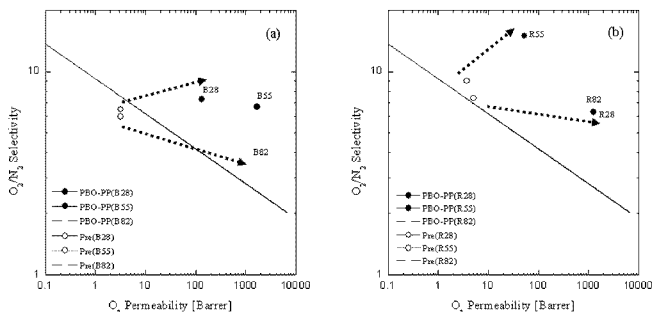


Fig. 2. O_2 Permeability and O_2/N_2 selectivity of (a) b-PBO-PP and (b) r-PBO-PP

The O_2 permecability and O_2/N_2 selectivity were shown in Fig. 2. The functionalized polyimide lies on the upper bound line proposed by Robeson. After thermal rearrangement, we found that the permeabilities and the selectivities of r/b-PBO-PP copolymers surpassed the separation limitations of conventional polymer by enhancing molecular sieving effect. In the case of block copolymer, the O_2 permeability increased as the mole fraction of PBO increased. However, the O_2/N_2 selectivity showed inverse tendency. The O_2 permeability of random copolymer was somewhat arbitrary. The r28-PBO-PP showed the highest O_2 permeability and the r55 PBO PP showed the highest gas selectivity.

4. Conclusions

Ultrahigh permeable r/b PBO PP copolymer gas separation membrane were successfully synthesized by thermal treatment at 450 °C. These materials showed high thermal stability and chemical resistance. Besides the O₂/N₂ separation process, these polymeric membranes can be used in various gas separation processes with more harsh conditions.

Reference

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