

폴리이미드실록산의 화학적 구조에 따른 탄소-실리카막의 미세기공 구조 특성에 미치는 영향

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Effect of Chemical Structure of Poly(imide siloxane) on Properties of Microporous Carbon-Silica Membranes

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1. Introduction

Among the various membrane materials, carbon molecular sieve membranes (CMSM) have numerous advantages compared with polymeric membranes [1]. Previous studies on CMSMs have focused on kinds of precursors and pyrolysis conditions (pyrolysis temperature, pyrolysis protocol, heating rate, and pyrolysis atmosphere) [2]. In contrast to common polymeric precursors, the role of each domain in imide siloxane copolymers is somewhat different from each other in regard to gas permeation through their pyrolyzed products, That is, carbon-silica materials consisted into two phases, such a carbon rich phase derived from polyimide and a siloxane rich phase derived from poly(imide siloxane).

In this study, we investigated the effect of chemical structures of poly(imide siloxane) on the properties of porous carbon-silica membranes and measured the gas separation properties using small gas molecules.

2. Experimental

Poly(imide siloxane) (Si-PI) copolymer was synthesized using BTDA, ODA, and PDMS. The chemical composition of BTDA/ODA/PDMS was 10/8/2 by mmol for the Si-PI. Firstly, PDMS was dissolved in tetrahydrofuran (THF, Aldrich Chem. Co., Milwaukee, WI, USA) and then *N*-methylpyrrolidinone (NMP, Aldrich Chem. Co.,

Milwaukee, WI, USA) solution of ODA was added. Finally, powder of BTDA was added to THF/NMP solution of PDMS and ODA, and then the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 6h to obtain homogeneous siloxane-containing poly(amic acid) (Si-PAA) solution. The Si-PAA solutions were cast onto a glass plate and then thermally imidization at 250 °C. For the carbon-silica membranes, poly(imide siloxane) precursors were pyrolyzed at 550, 600, and 700 °C, respectively.

3. Results and Discussion

Fig. 1 shows the thermal properties of poly(imide siloxane) precursor. Poly(imide siloxane) exhibited two-step weight-loss curves. From the results, the first weight-loss appeared by the decomposition of BTDA-PDMS segments, and the second weight-loss was caused by the decomposition of BTDA-ODA segments.

The gas permeabilities and selectivities of carbon-silica membranes were measured as a function of pyrolysis temperature. The gas permeabilities and selectivities of carbon-silica membranes derived from poly(imide siloxane) shows in

Fig. 2 and Fig. 3. For all carbon-silica membranes, the gas permeabilities of the selected gases were in the order He > CO₂ > O₂ > N₂. In general, the permeabilities of smaller gases through CMS membranes are consistent with the order of the kinetic diameters of the gas molecules [He (2.6 Å) > CO₂ (3.3 Å) > O₂ (3.46 Å) > N₂ (3.64 Å)]. From the results, the permeabilities of carbon-silica membranes decreased with higher pyrolysis temperature while the selectivities increased. In particular, the carbon-silica membranes pyrolyzed at 600 °C showed O₂ permeability of 736 barrer [$1 \times 10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s cmHg}$] and O₂/N₂ selectivity of 10.

Fig. 4. shows the O₂ permeabilities versus the O₂/N₂ selectivities of the carbon-silica membranes prepared in this study. As shown in Fig. 4, the permeabilities and selectivities of carbon-silica membranes significantly affected by the chemical structures of poly(imide siloxane).

4. Conclusions

In this study, we studied the effect of chemical structures of poly(imide siloxane) on the properties of porous carbon-silica membranes. The properties of

porous carbon-silica membranes significantly affected by the structural characteristics of poly(imide siloxane) and related to the enhancement of their gas permeabilities and selectivities. In conclusion, the gas separation properties of carbon-silica membranes could be controlled by the tuning the chemical structures as well as the pyrolysis conditions.

Acknowledgement

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References

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2. H. B. Park, I. Y. Suh and Y. M. Lee, Novel pyrolytic carbon membranes containing silica: preparation and characterization, *Chem. Mater.*, 14 (2002) 3034.

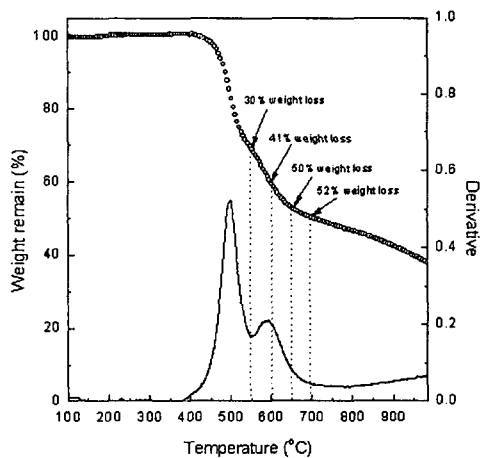


Fig. 1. TGA curve of poly(imide siloxane)

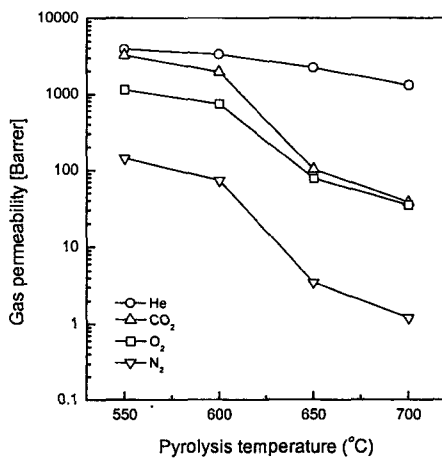


Fig 2. Gas permeabilities of carbon-silica membranes as a function of pyrolysis temperature

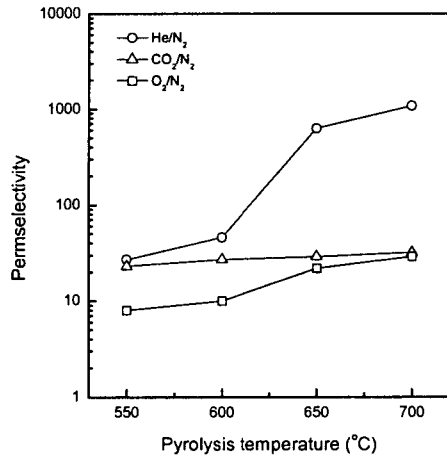


Fig. 3. Selectivities of carbon-silica membranes as a function of pyrolysis temperature

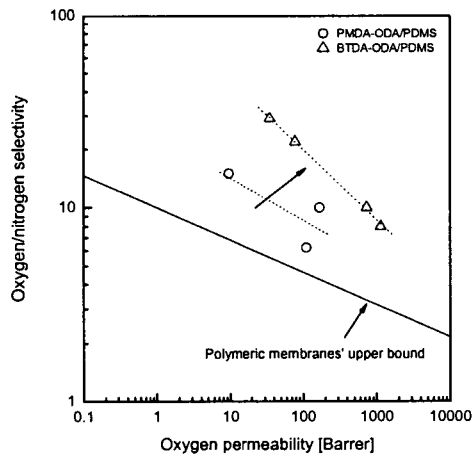


Fig. 4. O₂ permeabilities vs O₂/N₂ selectivities of carbon-silica membranes