APTEOS 하이브리드 멤브레인에서 PEG가 기체투과 특성에 미치는 영향

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The effect of PEG on gas permeation properties for APTEOS hybrid membrane

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INTRODUCTION

Polymers have been used for various applications because of their transparency, easy processability, flexibility, lightness, and so on. However these have poor thermal stability, high permeability of water vapor and gases, and UV transmission. On the other hand, inorganic materials have high thermal and mechanical strength and low gas permeability. It is thus possible to prepare new kinds of materials that have advantages of both organic and inorganic materials. Over the past decade, the development of the gas separation process using inorganic membranes has attracted a great deal of interest. This has primarily been due to the new separation opportunities provided by the improved thermal and chemical stability over that of the commercially more advanced organic membranes. The applications provided by this include the employment of membranes in catalytic reactors, enhanced oil recovery and gas sweetening, and the separation of flue gases.

Hybrid organic-inorganic materials with a potential interest for membranes can be classified in three categories. Type Ⅰ deals with materials exhibiting interactions like van der Waals forces or hydrogen bonds between organic and inorganic parts. Type Ⅱ consists in materials with covalent bonding between organic and inorganic parts, resulting in a homogeneous hybrid material at the molecular level. Type Ⅲ hybrid organic-inorganic membranes can be described as organically modified ceramic membranes. In general, such membranes with grafted organic groups result from surface modification using plasma polymerization techniques, or coupling agent able to react with the hydroxyl groups present on the ceramic oxide surface.

Recent efforts have been focused on producing organic-inorganic hybrid membranes using organosilicate precursors to form microporous silica network systems. Tamaki et al.[1999] homogenously incorporated poly(N-vinylpyrrolidone) with a silica gel, using a sol-gel process. Methyl triethoxysilane(MTMOS) was used as the organosilicate precursor because the methyl group prevented complete hydrolysis and provided a less crosslinked and more flexible gel. Smaihi et al.[1999] prepared hybrid imide-siloxane copolymers by sol-gel coreaction of pyromellitic dianhydride, aminoalkoxysilane and tetramethoxysilane(TMOS). In this experiment, aminoalkoxy-silane was used to provide a bonding between the inorganic and organic phases.

In the present work, hybrid sols were synthesized by the addition of PEG to a APTEOS in ethanol solution. When APTEOS was used only coating material, extremely dense membrane was obtained, and It had very low gas permeabilities[]. In order to higher permeability coefficients and selectivities than APTEOS membrane, PEG was added in APTEOS solution. Therefore, pore size could be controlled by addition of PEG. The gas permeation properties of the hybrid membranes have been investigated and the results are discussed in relation to the molecular weight and content of PEG.

EXPERIMENAL

3-aminopropyl triethoxysilane(APTEOS)[Aldrich, 98%] was mixed in ethanol with molar ratio of 10. After water was added to the mixture, this mixture was stirred room temperature. The molar ratio of water to APTEOS was 3, stoichiometrically. Adding polyethylene glycol, the mixture was stirred continuously in a closed container. The solution was cast on asymmetric porous support of polysulfone(PSf), and polyvinylidene difluoride. The obtained composite membrane was dried at room temperature and 90℃ for several days, and then kept in the desiccators before the characterizations. The composite membranes were characterized by various methods, such as Fourier transform infrared(FT-IR, JASCO-430) and ^{29}Si nuclear magnetic resonance(^{29}Si-NMR, Varian UI-200) spectroscopy. The morphology of cross-section and surface of the coating films were characterized with the scanning electron microscopy (SEM, JEOL, JSM-5310LV). A constant volume-variable pressure method was used to determine steady state permeability coefficients at 30℃ and 1atm of upstream pressure. The membrane was mounted on the permeation cell and degassed by exposing both sides of the film to vacuum. The steady-state rate of pressure rise in a downstream receiving volume was used to determine the gas permeability coefficient. The permeation apparatus is shown schematically in Fig. 1. At steady state the following expression was used to calculate the permeability coefficient.

$$P = \frac{22{,}414V}{RT\frac{p_1}{l}} \frac{dp_2}{dt}$$

Where V is the downstream reservoir volume, p_1 is the upstream pressure, A is the cross sectional area, l is thickness of the membrane, and dp_2/dt is the rate of change in downstream pressure.

RESULT AND DISCUSSION

When APTEOS was used as only coating materials, homogeneous and uniform thin films

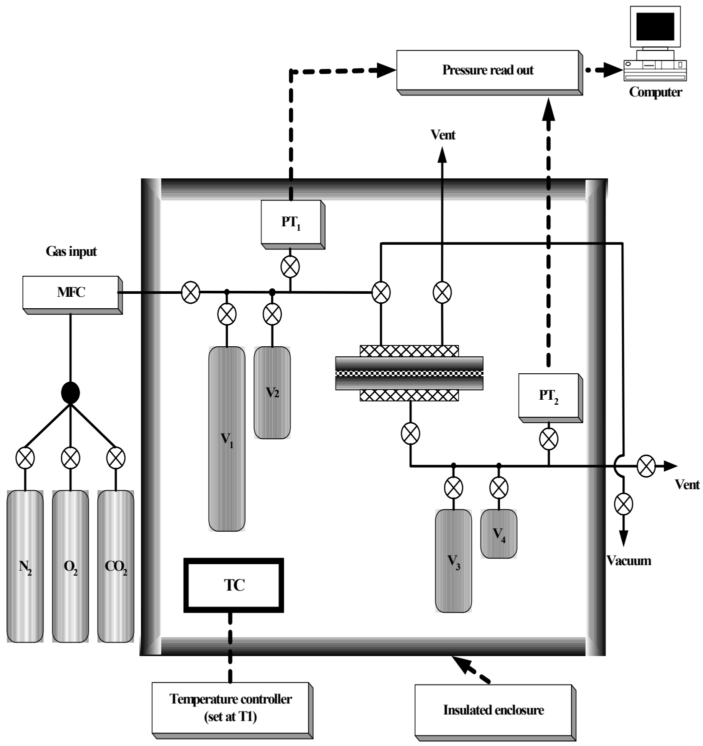

Fig.1 The schematic diagram of permeation apparatus

without cracks were obtained in the previous study, and showed very good barrier properties. The Fig.2 represent permeability coefficient of nitrogen, oxygen and carbon dioxide, respectively, and show that the gas permeability coefficient of PP substrate coated with APTEOS depend on the water ratio and storage time. Open square symbols in fig.2 represent PP substrate's gas permeability coefficient, and closed square and circle symbols represent that of water ratio 1 and 3, respectively. The coating of APTEOS is very effective to suppress the gas permeation. This may cause the formation of dense structure and good adhesion between APTEOS layer and PP substrate. Membranes prepared on the PSf substrate with the sols were quite brittle. Therefore, it was necessary to restrict the measurements to samples with the sols and prepare the membranes with PEG. The addition of PEG to APTEOS sols was possible to control the pore size and give flexibility to membranes. Although, the homogeneous and uniform membranes without cracks were obtained by addition of PEG, It shows very low selectivities and high permeabilities. Because, It has problem with affinity between coating layer and substrate. The gas permeability measurements of membranes, prepared using substrate having a good affinity for coating layer, were carried out using pure nitrogen, oxygen and carbon dioxide, respectively. The results show that the hybrid membrane prepared using APTEOS and PEG has good gas permeability coefficient and selectivity.

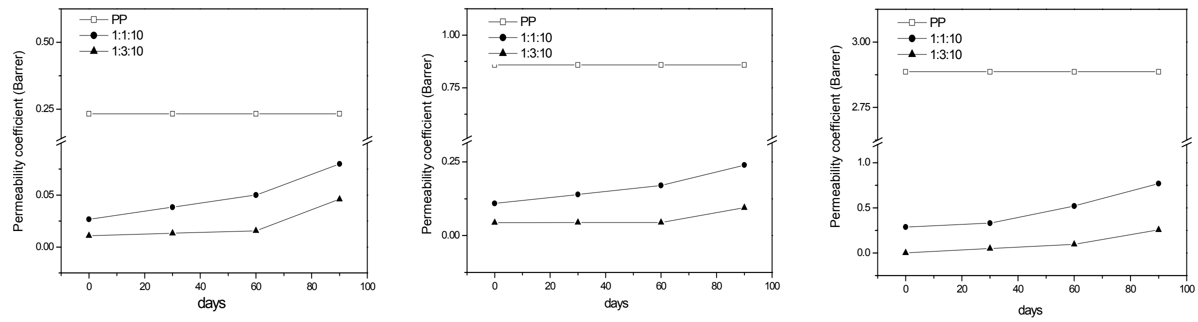

Fig.2 The permeability coefficient of (a)nitrogen, (b)oxygen, and (c) carbon dioxide as a function of storage time

CONCLUSIONS

Hybrid organic inorganic membranes were prepared by APTEOS and PEG. All the samples were transparent, and homogeneous with crack-free. The gas permeability coefficient of polyvinylidene difluoride film was measured considerably by the coating of APTEOS and PEG. The addition of PEG increased the diffusivity of nitrogen, oxygen, and carbon dioxide. It might be concluded that good good gas permeability coefficient and selectivity of hybrid membranes due to the formation of dense structure and good adhesion between hybrid layer and substrate

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