

Trichloroethylene/water의 투과증발을 위한 새로운 copolyimide 막

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New Copolyimide Membranes for Pervaporation of Trichloroethylene from Water

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1. Introduction

Hydrophobic rubbery polymers are good candidates for VOC permselective membranes. In particular, PDMS has been widely studied in this respect, because PDMS has a high selectivity and permeability to organic chemicals over water [1]. The high selectivity and permeability of PDMS originates from its excellent affinity for VOCs due to its hydrophobicity and its low diffusion resistance to VOCs due to its flexibility. However, although PDMS membranes possess the above advantages, they have poor mechanical strength and film-forming properties, and therefore, their application has been restricted. To improve the mechanical properties of PDMS, effort has focused on developing new PDMS-based membranes employing chemical crosslinking and chemical modification, or by blending PDMS with other materials. In particular, aromatic polyimide-containing PDMS materials, such as polysiloxane-imide homopolymers, and PDMS-polyimide block or graft copolymers have been studied by many researchers [2-4], because polyimides are known for their excellent thermal stability, chemical resistance, and mechanical strength.

We have previously prepared tough homopolyimides with fluorinated side groups [5] that showed good permeability and selectivity towards VOCs over water due to

their hydrophobic and bulky side group structures. Since these polyimides have the potential for improving the mechanical properties of conventional polysiloxane membranes without sacrificing any permselectivity, we have carried out an intensive effort to combine fluorinated polyimides with PDMS.

We have prepared a series of new copolyimides, in which the fluorinated rigid groups and the flexible PDMS groups are incorporated by polycondensation of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), diamine-terminated polysiloxane (SIDA), and 2-(perfluorohexyl)ethyl-3,5-diaminobenzoate (PFDAB). With the aim of developing pervaporation membranes with a high separation capability of hydrophobic VOCs from contaminated water, the physical properties of polyimides with different SIDA/PFDAB ratios and their pervaporation behavior with aqueous TCE mixtures were investigated in terms of solution-diffusion theory.

2. Experimental

2-1. Polymerization and membrane preparation : Two homopolyimides, 6FDA-PFDAB (PFDAB 100) and 6FDA-SIDA (SIDA 100) were prepared as described in previous publications [6]. Three types of copolyimide with different SIDA/PFDAB ratios (mol/mol = 25/75, 50/50, and 75/25) were synthesized using a one-pot imidization process. A prescribed mass of SIDA/PFDAB diamine monomer was dissolved in 50 ml of THF using a magnetic stirrer, under flowing N₂ gas. The reaction was monitored using a thermometer, and carried out using a condenser. An equimolar mass of 6FDA was subsequently added, the mixture stirred for 4 h at room temperature to yield a homogeneous polyamic acid solution, and then, 50 ml of NMP/toluene (1:1 v/v) was then added to the mixture. The concentration of monomer was maintained at 15 wt%. The reaction temperature was gradually heated to T = 190 °C and allowed to remain at this temperature for 15 h, resulting in a highly viscous polyimide solution. The solution was then cooled, and a 20-fold excess of methanol was added drop wise with vigorous stirring, causing the polyimide to form a precipitate. To obtain the pure polymer, the above precipitation procedure was carried out three times. The precipitate was then separated by filtering and dried at T = 120 °C. The resulting polymer was dissolved in THF (10 wt%), cast onto a Teflon plate, and dried in a vacuum oven to yield the desired polyimide membrane.

2-2. Physical property measurements : A ¹H-NMR spectrometer (DRX300, Bruker, USA), in which tetramethylsilane (TMS) was used as an internal standard, and an ATR/IR spectrometer (Digilab, Model FTS-80, Bio-Rad, USA) were used to

monitor the progress of reaction. Dynamic mechanical measurements were performed using a dynamic mechanical analyzer (DMA; DuPont 2980, USA) operating at $f = 10$ Hz and using a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The d-spacing (d) of the membrane samples was monitored using an X-ray diffractometer (Model D/MAX IIIB, Rigaku, Japan) operating at a wavelength of $\lambda = 1.54\text{ \AA}$. The intrinsic viscosity (η_{int}) of 0.5 g/dl^{-1} of polymer in THF at $T=30\text{ }^{\circ}\text{C}$ was determined using a Cannon-Fenske viscometer. The density of the polymer was measured using the buoyancy method employing a micro-balance. The fractional free volume (FFV) was determined using group contribution theory. The total surface free energy was calculated using the Young-Wu equation from contact angle data measured using the sessile drop method employing a Rame-Hart goniometer (Erma Model G-1, USA) using water and methylene iodide as the contacting liquids.

2-3. Pervaporation measurements : The pervaporation apparatus, which was also used in previous studies, was composed of a cell in which the polymeric membrane was placed on a porous stainless steel metal support, and had a circulation pump to agitate the feed, cold traps to condense the permeate, a vacuum line, and an on-line GC with a thermal conductivity detector (TCD) and a Porapak R column. The effective membrane area in contact with the feed was 13.85 cm^2 . The pressure at the permeate side was maintained at $P < 2$ torr, and the feed temperature was fixed at $T=25^{\circ}\text{C}$. The membrane thickness was about $50\text{ }\mu\text{m}$, and the organic TCE concentration in the water was $0.05\text{ wt}\%$.

3. Results and Discussion

3-1. Preparation of polyimides : Five polyimides were prepared from dianhydride monomer, 6FDA, and two diamine monomers, PFDAB and SIDA, using a direct (one-pot) imidization process. THF solvent was used for the preparation of the copolyamic acids, because the commonly used aprotic solvents, such as NMP, DMF, and DMAc are not suitable for these compounds, due to the poor solubility of the SIDA moieties in the polyamic acids. All the polymerizations proceeded in the homogeneous solutions, and the progress of the reaction was easily confirmed by the increase in solution viscosity during the polymerization. The intrinsic viscosities of the polymers ranged from $0.55\text{-}0.82\text{ dl/g}$, which meant that the molecular weights of the polyimides were high enough for the preparation of the tough polymer membranes. The viscosity values generally increased with higher SIDA content, probably because the SIDA moieties had higher molecular weights than the PFDAB.

3-2. Pervaporation properties of the polyimide membranes : Figure 1 shows the permeation flux and selectivity of the membranes plotted as a function of the SIDA/PFDAB ratio in the polymers. Any transitional behavior from an organic TCE-selective to water-selective membrane was not observed. The permeation flux and selectivity of the organic solution increased with increasing SIDA content because of the higher solubility and diffusivity of TCE over water in the siloxane moieties, as discussed above. This indicates that even traces of organic TCE at 0.05 wt% in water can be efficiently collected using these membranes because of their high selectivities. As expected, sample SIDA50-PFDAB50 showed the enhanced mechanical stability and excellent pervaporation performance compared with the SIDA100 membranes.

4. Conclusions

A series of polyimides were prepared by polycondensation of flexible siloxane diamine and rigid fluorinated diamine with 6FDA, and their physical and pervaporation properties were characterized according to the ratio of diamines. The SIDA-rich polyimides exhibited lower densities and surface free energies, but had higher fractional free volumes and d-spacings than the PFDAB-rich polyimides. It was found that all the polyimides were amorphous, and that the SIDA-containing polyimides exhibited double glass transition temperatures, indicating microphase-separated morphologies. As the SIDA/PFDAB ratio decreased, the polyimides became mechanically more stable. As the SIDA/PFDAB ratio increased, the sorption and diffusion of TCE over water increased markedly, and thus, the permeation flux and pervaporation selectivity of the polyimide membranes increased markedly. This correlated well with the increased FFV values and the lower surface free energy. The SIDA50-PFDAB50 copolyimide membranes showed excellent separation capability for aqueous TCE mixtures with an enhanced mechanical stability.

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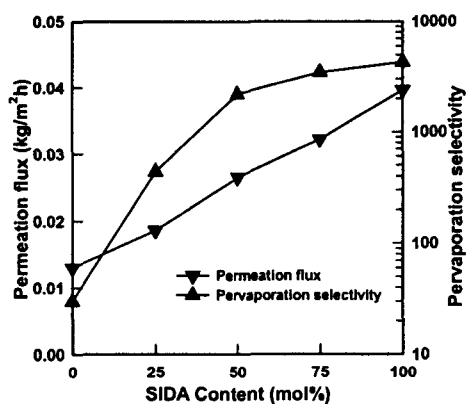


Figure 1. Permeation flux and permeation selectivity of the polyimide membranes at T = 25 °C as a function of the ratio of SIDA:PFADAB.