3E4) VOC/Gas, Gas/Gas Separation Performance of Nanostructured Polydimethylsiloxane/Silica Hybrid Membrane

De-Lin Xu · Bum-Suk Jung[1] · Yong-Soo Kang[1] · Wook-Jin Chung · Eun-Mi Gwon
Department of Environmental Engineering and Biotechnology, MyongJi University
[1]Center for Facilitated Transport Membranes , Korea Institute of Science and Technology

1. Background

Membranes and separations have become a multimillion dollar industry, growing at a rate of 10% to 20% per year. Now, the focus of research and development has shifted to the modification of the surface rather than the alteration of the basic polymer type or inorganic substrate.

For the recovery of VOCs, organophilic rubbery membranes are preferred because they are much permeable to VOCs. Among the rubbery membranes, poly(dimethylsiloxane)(PDMS) exhibits an excellent membrane performance for the removal of VOCs from noncondensable gases; high permeability and high selectivity for VOCs.

The effect of introduction of fumed-silica particles into organic polymeric membranes for gas separation processes have attracted a great deal of interest, because the addition of inorganic particles can enhance mechanical toughness, and separation performance of the membrane.

2. Materials and Methods

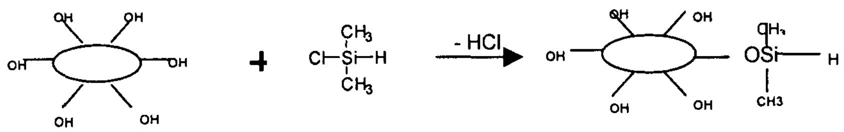
Dense and composite PDMS/silica hybrid membranes were prepared for this study. The PDMS polymer is generously supplied by Dow Corning company. It's composed of two parts: part A and part B. Main component of part A is dimethylvinyl-terminated polydimethylsilane, part B is the crosslink agent which is formed by pt-based catalyst.

Information of fumed-silica

Fumed-silica type	Silica content	Surface groups	Surface area	Particle size
M-5	99.8%	-OH	200(m^2/g)	14nm

(supplied by Sigma company)

In our experiment, wesuccessfully prepared the uniformed hybrid polydimethylsiloxane(PDMS)/ fumed-silica membrane system by the process of surface modification to the fumed silica. This was achieved by the reaction between the hydroxy group on the silica surface and chlorodimethylsilane (CDS) reagent.



The IR spectra results (Figure 1), shows that the original hydrophilic nano-scale silica (A) were changed into the hydrophobic one(B). Conversion of surface Si-OH to Si-OSiH(CH_3)$_2$was observed by the completely disappear-ance of absorptionpeaks at 3433, assigned to Si-OH bond vibrations, and by the appearance of the absorption peaks at 2973, 2149, 914, assigned to C-H, Si-H, O-Si(CH_3) bond stretching vibrations respectively.

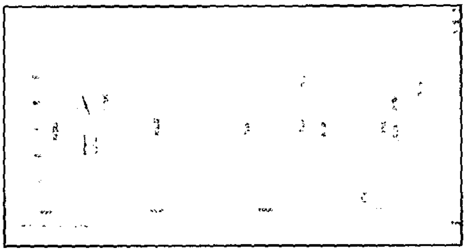


Fig. 1. IR spectra resu

Homogeneous dense PDMS/silica hybrid membranes were prepared by radical crosslinking between PDMS oligomer (part A) terminated with vinyl groups and a mixture of Pt catalyst(partB), then hybrid it together with the modified silica. Dissolving modified silica in toluene, after sonification, adding PDMS part A and part B as a ratio of 10:1, prepared a casting solution. The casting solution was poured into a Teflon Petri dish and then allowed to dry in a fume hood for several hours, and then, place it in the vacuum oven for one day for complete curing.

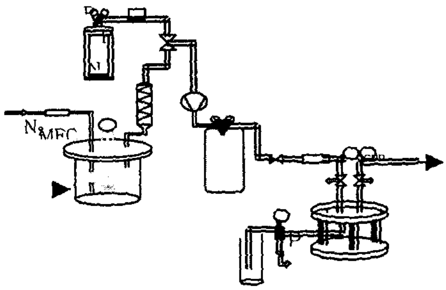


Fig. 2. Schematic diagram of separation apparatus

In the case of composite membrane, the active PDMS layer was casting on the surface of polysulfone membrane by the operation of Mayer-bar coating machine. By employ different color of Mayer-bar, the thickness of coating membrane could be controlled.

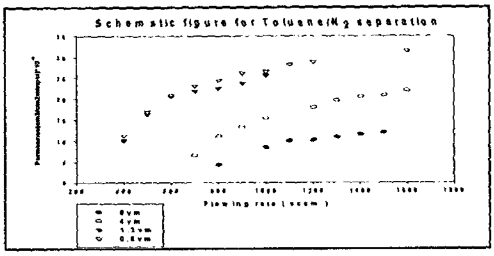


Fig. 3. Toluene/N_2 separation performanc

The total membrane separation apparatus is composed of three parts: feeding system, membrane cell, and data acquisition system, shown in Figure 2. The feeding system including a vapor generator was designed to produce a certain composition ofr vapor/gas mixture. The vapor generator was equipped with a mass flow controller and a pressure regulator so that thecomposition of the produced mixture was able to be controlled precisely by adjusting the flow rates ofthe first and second N_2 streams and pressure. The first N_2 stream was introduced to the vapor generatorfilled with a liquid VOC to be vaporized. This stream was then mixed with the second stream of pure N2 to produce a mixture stream of a desired composition and flow rate. The membrane cell was made of stainless steel. Shimadzu-GC 14B is used for testing the membrane inlet, outlet and permeate concentration.

3. Results

Generally, the permeation of permeants through the rubbery membrane is characterized as a sorption controlled process, so the sorption behavior of a permeant could determine significantly permeation and separation performance. The greater the affinity of a permeant towards a membrane is, the higher the solubility of the permeant in the membrane is. VOC/N_2 separation experiment was done by employing PDMS/PS composite membranes in various coating thickness. With the increasing of the inlet flowing rate, the permeance and permeability can be increased apparently. In the case of permeance, thevalue is related with the thickness of the membrane.

The pure and mixed-gas permeation properties of the PDMS/silica hybrid membrane were studied. The gas permeability (Fig. 4) and selectivity (Fig. 5) increased simultaneously as the filler content increased. The oxygen and nitrogen permeability were increased 2-3 folds whenthe silica content increased by 30% compared with the pure sylgard 184 PDMS dense membrane. In addition, the selectivity of O_2/N_2 also increased apparently. From the AFM, X-ray and Tg test results, it can be noted that, the modified silicas can exist homogeneously with PDMS polymer, by adding the inorganic silica particles, the glass transition temperature increased. The improvement of gas permeability and selectivity is because of the enhancement of free volume among the polymer chain packing.

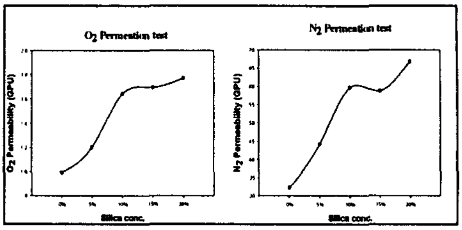


Fig. 4. Pure gas permeability of silica hybrid membrane

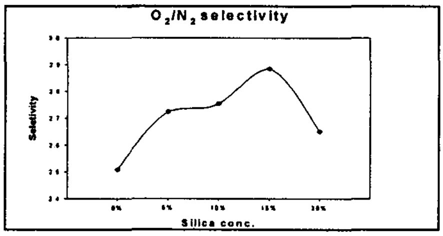


Fig. 5. Gas selectivity of silica hybrid membrane

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