

Separation of Hydrogen-Nitrogen Gas Mixture by PTMSP-Silica-PEI Composite Membranes

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1. Introduction

Organosilicon polymers have long paid attention as functional polymers [1,2]. Among others, poly-(1-trimethylsilyl-1-propyne) [PTMSP] is a polymer, which forms a gas separating membrane with extraordinary high gas permeability. In particular, composite membranes that constituted two different matrices (inorganic and organic) have been recently developed in order to improve the permeation characteristics. They are described as presenting the advantages of each material in a single membrane. When the interactions between the polymer and the filler are important, the gas permeability and diffusion coefficient decrease with the content of filler. Many other authors have been studying the effect of fillers when the fillers have the properties of adsorbents or shape-selective materials. Such fillers are generally used in the polymeric matrix in order to form a heterogeneous membrane. As a result, such membranes are able to improve the separation properties of polymers for gas separation [3,4]. In this work, we present the permeation properties of the mixed gas, H₂/N₂ on the PTMSP-silica-PEI composite membranes.

2. Experimental

2.1. Polymer Synthesis

PTMSP sample was synthesized as described earlier [2]. 1-Trimethylsilyl-1-propyne (Aldrich Chemicals) was polymerized using TaCl₅ (99.9% purity, Aldrich Chemicals) as catalyst. Polymerization was carried out in the glass reactor under argon atmosphere with the following condition. Monomer/catalyst ratio equals to 60. A solution of 0.36g of TaCl₅ in 50ml toluene was stirred at 80 °C until complete dissolution of TaCl₅. Thereafter, 8.85ml of 1-trimethylsilyl-1-propyne was added to the catalyst solution, and the mixture was reacted for 1h at 80 °C. The viscosity of the solution increased very rapidly. The polymer formed was dissolved in toluene (500 ml) with being stirred under argon, which was then precipitated into a large amount of methanol. After filtration, the polymer flakes were washed two times with methanol, and dried under vacuum.

2.2. Polymer membrane preparation

PTMSP membrane was prepared by casting from a toluene solution (2 wt% polymer) on porous polyetherimide (Aldrich Chemicals) support. The membrane was dried under vacuum at 60 °C for one day. Silica-filled PTMSP membranes were made by dispersing 23-60 wt% (based on polymer content) silica particles in the PTMSP solution. The dispersion was mixed with a high-speed blender for one day and cast on porous polyetherimide (Aldrich Chemicals) support. The silica-filled PTMSP membranes were dried as described above.

2.3. Gas permeation measurements

The gas permeation properties of PTMSP and silica-filled PTMSP membranes were determined with a gas mixture containing 32mol% H₂/68mol% N₂. The experiments were

measured at different pressures($\Delta P= 5-30$ psi) and constant temperature(25°C).

3. Result and discussion

3.1. Characterization of membranes

The IR spectra of PTMSP and silica are shown in Fig. 1. A comprehensive work on the IR spectrum of PTMSP is found in [5]. In the IR spectra, the band at about $970 - 980\text{ cm}^{-1}$, which is attributed to silanols that exist on the silica and not on PTMSP, can be evaluated to trace silica on the membranes [6]. The band at 1246 cm^{-1} , which is assigned to the CH_3 symmetric deformation of the Si (CH_3) groups [5], is very deep on the spectrum of the PTMSP membrane, without silica. Fig. 2 shows the same band, however not so sharp, still exists on the spectra of the PTMSP membrane containing different amounts of silica. The SEM pictures taken from the PTMSP-silica surface and from the cross section of the membranes are represented in Figs. 3 and 4. The particle size of silica increases as silica content of the membrane increases from 23 wt% to 47 wt%. In contrast to this, the particle size of silica decreases in the range of 54 ~ 60 wt% silica-filled PTMSP membranes, and a uniform distribution of the silica is observed. The PTMSP-silica layer that was observed on the cross sections of the membranes is about 5 to 12 μm thick layer. The total thickness of PTMSP-silica-PEI composite membrane was measured with a precision micrometer. The composite membranes with thickness of $\sim 140\text{ }\mu\text{m}$ were used for the permeation measurement.

3.2. Mixed-gas permeation properties of the silica-filled PTMSP membranes

The effect of silica loading on the real separation factor(α) of H_2/N_2 for PTMSP-silica-PEI composite membranes is shown in Fig. 5. The data show that the real separation factor of H_2/N_2 increased as the pressure of permeation cell and silica content of the membrane increased. The increasing selectivity with increasing silica content is not only due to a molecular sieving mechanism, considering the kinetic diameters of the gases, but also depend on the microstructure of the membranes. The real separation factor was 1.3 for pure PTMSP, but increased to 2.0 for 60 wt% silica-filled PTMSP at ΔP 30psi and 25°C .

4. Conclusions

Since the permeability and the selectivity of the PTMSP membrane can be changed by modification, the introduction of the silica to produce PTMSP-silica-PEI composite membranes was examined in the present study. The real separation factor of H_2/N_2 increased as the pressure of permeation cell and silica content of the membrane increased.

References

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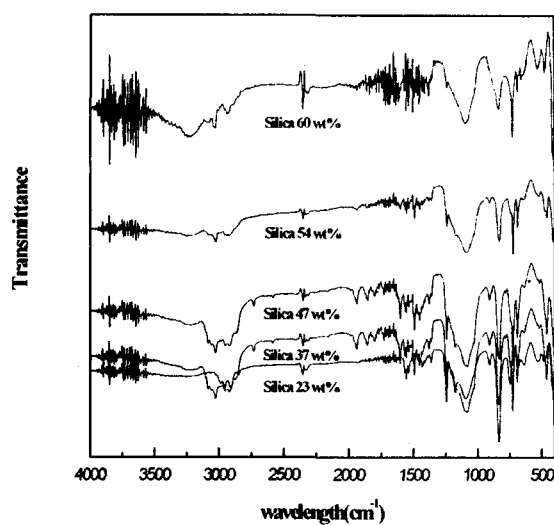
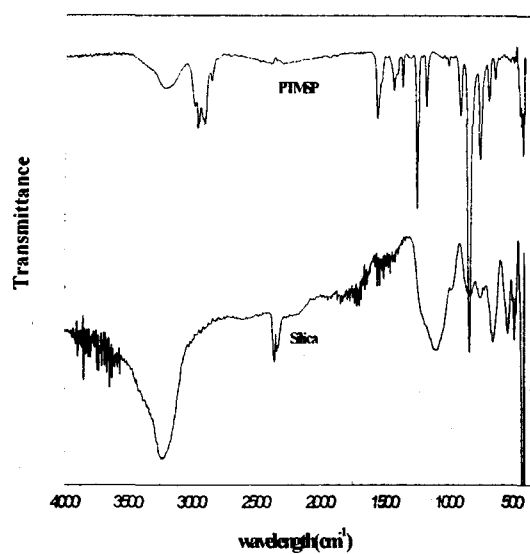


Fig. 1. FT-IR spectra of PTMSP and silica. Fig. 2. FT-IR spectrum of PTMSP-silica composite membranes.

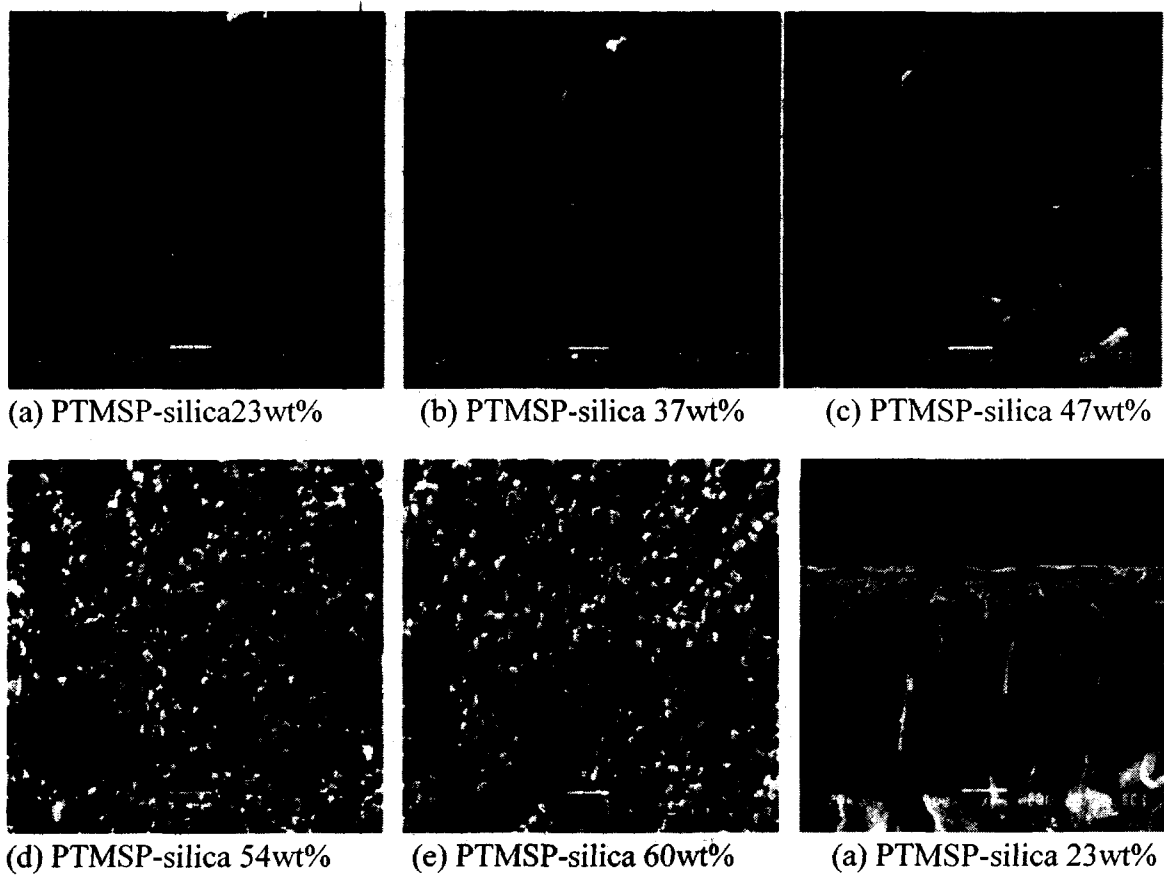
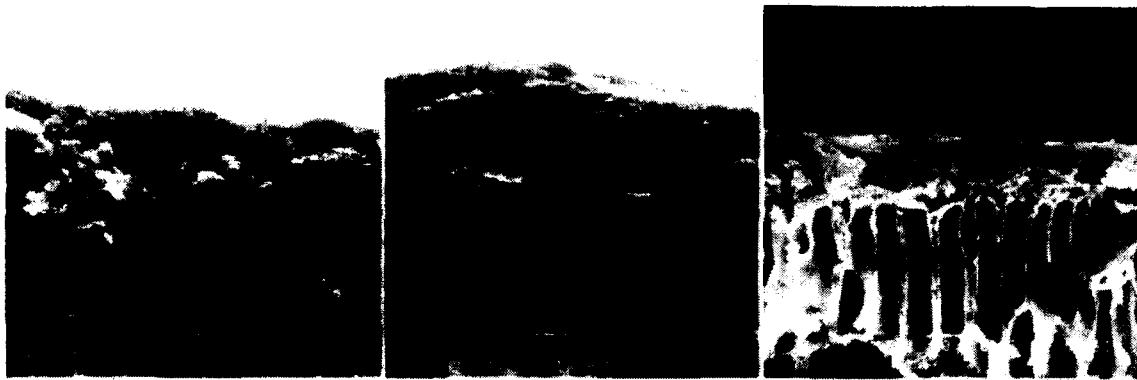


Fig. 3. SEM micrographs of the surface of PTMSP-silica-PEI composite membranes.

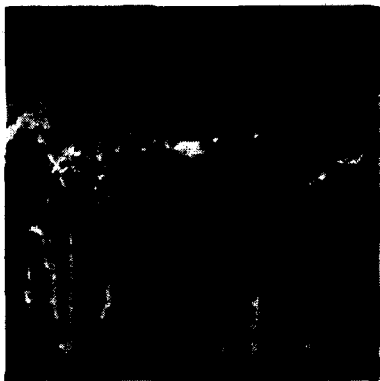


(b) PTMSP-silica 37wt%

(c) PTMSP-silica 47wt%

(d) PTMSP-silica 54wt%

Fig. 4. SEM micrographs of the cross-section of PTMSP-silica-PEI composite membranes.



(e) PTMSP-silica 60wt%

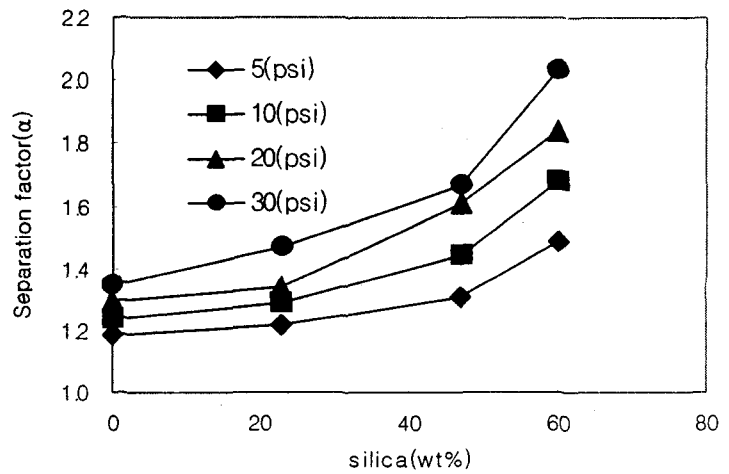


Fig. 5. Effect of silica loading on the real separation factor of for PTMSP-silica-PEI composite membranes.