The flow of CO_2 and N_2 gases through Asymmetric Polyetherimide Membrane

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Abstract

The asymmetric hollow fiber membranes were prepared by the wet spinning of polyetherimide dope solution and the effect of hollow fiber structures on the permeation characteristics of carbon dioxide and nitrogen gases through these membrane were investigated. As the concentration of the γ-butyrolactone (GBL) in dope solution, acting as a swelling agent was increased, the strucutre of hollow fiber was changed from the finger to sponge type. The permeabilities of gases (CO_2, N_2) through these membrane were measured over the wide range of pressure under different temperature. The effect of water vapor on the permeabilities of gases was also investigated. The measured permeabilites showed the different characteristics depending on the structure of membranes. It was found that the flow through the pores were dominant over the polymers matrix. Blocking effect by water vapor in the pores of skin layer greatly improved the ideal separtion factor of carbon dioxide/nitrogen.

Keywords : polytherimide, asymmetric membrane,
gas permeability, blocking effect, water vapor

Introduction

The polyetherimide which is an amorphous themoplastic resin and shows good mechanical strength and high thermal resistance has been known as a good material for separating membranes especially for the gas separation.

With this reason some researches with polyetherimide have been done for the separation of the carbon dioxide[1,2] and the helium gas [3].

In our research group the asymmetric polyetherimide hollow fiber membranes as a base material have been prepared by the wet spinning for the development of high selective CO_2/N_2 separation membrane.

The structure of these asymmetric type membrane prepared by the phase inversion process were greatly affected by the composition of the dope solution, the composition of coagulant, the spinning condition and the post treatment condition [4-10].

Since the membranes prepared by this method usually have the micropores formed on the skin layer, the gas separation membrane is thin coated with other polymer becoming a composite membrane.

The gas permeability and selectivity of composite membranes were very dependent on the structure of the asymmetric layer.

In this research asymmetric polyetherimide membranes were prepared from the dope solution of different swelling agent concentration and the surface was modified by sodium hydroxide aqueous solution to control the pore structure of the skin layer.

The flows of CO_2 and N_2 through these membranes were studied under different pressures and temperatures.

For the high permselectivity of CO_2/N_2 the blocking effect of water vapor on the permeation of gases was also investigated.

Experimental

Materials

The polyetherimide (Ultem, Gerneral Electric Company) was used as a membrane material. N-methylpyrrolidone and γ-butyrolactone (GBL) were used as a solvent and a swelling agent withouth purification. Sodium hydroxide was used for the modification of the polyetherimide.

Preparation and Modification of Hollow Fibers

Two metering gear pumps of Cole Parmer Co. were used for the injection of dope solution and internal coagulant. The used nozzle was tube-in orifice type with inner diameter, 0.4mm outer diameter 1.2mm.

GBL was used as an internal coagulant and water was used as an outer coagulant.

The prepared hollow fiber membranes were modified by heating them in the 0.2 mole of aqueous sodium hydroxide solution at 60 °C

Gas permeation test

To measure the gas permeabilities, the hollow fiber membrane modules were made and kept in the constant water bath and the upstream pressure was changed over the wide range under different temperature.

For the study of water vapor effect, the upstream gases were saturated with water vapor by passing through the water reservior. The down stream pressure was kept at atmospheric pressure for the pressure mode and vacuum for the vacuum mode permeation.

Results and Discussion

Effect of GBL concentration on the hollow fiber structure

The polyetherimide hollow fibers with a outer skin layer were spun from the dope solutions containning different amount of the GBL as a swelling agent 0, 10 and 20 wt% respectively. The hollow fiber structure is changed from finger to sponge structure by the slow interchange of solvent and nonsolvent in the phase inversion process with increasing GBL concentrations in the dope solution.

Effect of pressure and temperature on the permeability

There are several possible ways for gases can permeate through these asymmetric microporous membrane ; gas phase and surface condensed flow through pores and activated diffusion flow through polymer matrix.

In gas phase flow, viscous flow or knudsem flow are dominent depending on the pressure of the flow gases and the pore size of the membranes, in other words, the ratio of mean free path of a gas to the diamater of the pores.

The permeabilities of CO_2 and N_2 through these hollow fibers spun from dope solutions of different GBL concentration were shown in Figure 1. The permeabilities of gases and their dependence on pressure were increased with increasing GBL concentration. This results could be explained by the increase of the porosity and the pore size of membranes which were formed during the slow interchange of solvent and nonsolvent in the phase inversion process with increasing GBL concentration.

The higher permeability of carbon dioxide than that of nitrogen is due to the good carbon dioxide selectivity of polyetherimid matrix by solution diffusion flow and the surface flow of carbon dioxide through micropores.

The dependence of CO_2 permeability on pressure is much larger than that of N_2 due to the plasticization of the membrane by dissolved CO_2 and surface flow through pores.

The dependence of N_2 permeability on pressure is mainly due to the viscous flow in gas permeation through relatively larger pores in the skin layer.

The permeabilities of CO_2 and N_2 at different temperatures, 25°C, 25°C, 75°C through hollow fibers were shown in Figure 2. All the permeabilities of CO_2 and N_2 were decreased with increasing permeation temperature.

These phenomena can be explained by the decrease of gas and surface flow through pores in active layer of asymmetric membranes.

These results show clearly that the combined flow of sevenal different flow mechanism working together in these membranes and the flows through the pores were dominant over the polymer matrix.

Effect of water vapor on the gas permeability

As the skin layer of asymmetric membranes contain smaller pores, the capillary condensation becomes more important for gas separation [11-15].

When a non condensible gas flow through microporous membrane with condensible vapors, very high separation factor can be obtained due to the blocking effect of the capillary condensate.

In this study blocking effect of water vapor for the gas permeability was investigated and some results were shown in Fig. 3 and Fig. 4.

As the small pores in membranes were blocked by the condensed water, the permeate rate of N_2 was much reduced and sometimes it was too small to measure by our measuring system. The permeability of CO_2 was also decreased 5-10 times but still had high values. This results could be explained by the difference of solubilities and diffusivities of two gases through condensed water phase in pores.

Some results were presented in Table 1 for the mixed gas of CO_2 and N_2 (20/80 wt%) gases. When the mixed gas of CO_2 and N_2 flow through these membranes with water vapor, the separation factor was not so high as expected. It was assumed that the dissolved CO_2 reduced the surface tension of condensate water and the blocked water film in large pores was easy to break by small pressure drop. For the stable condensate film, the pore size should be small enough.

The hollow fibers were modified by aqueous sodium hydroxide solution to reduce the pore size and make the surface of polyetherimide more hydrophilic [10].

The compared data between modified and non-modified membrane were shown in Table 2.

The selectivity of modified polyetherimid membrane was much higher than that of polyetherimide itself by keeping the condensate film stable in hydrophilic small pores.

Conclusion

The permeation properties of CO_2 and N_2 through the asymmetric polyetherimide hollow fiber membranes of different structure were explained by the combination of the gas and surface flow through pores and the activated-diffusion flow through polymer matrix. The blocking effect of the water vapor on the permeation of gases was very significant and can be used for the separation of CO_2 and N_2.

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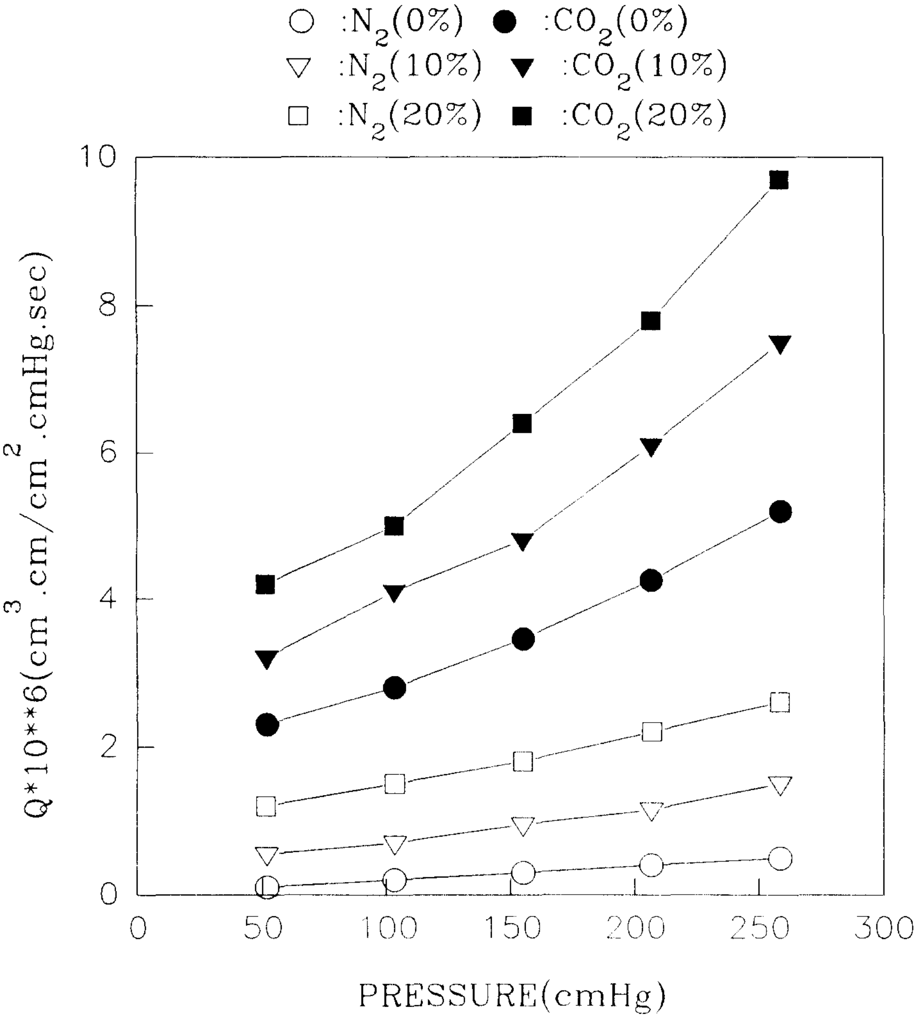

Fig. 1. Gas permeabilities vs. pressure through the hollow fiber membranes of different GBL concentration(70°C)

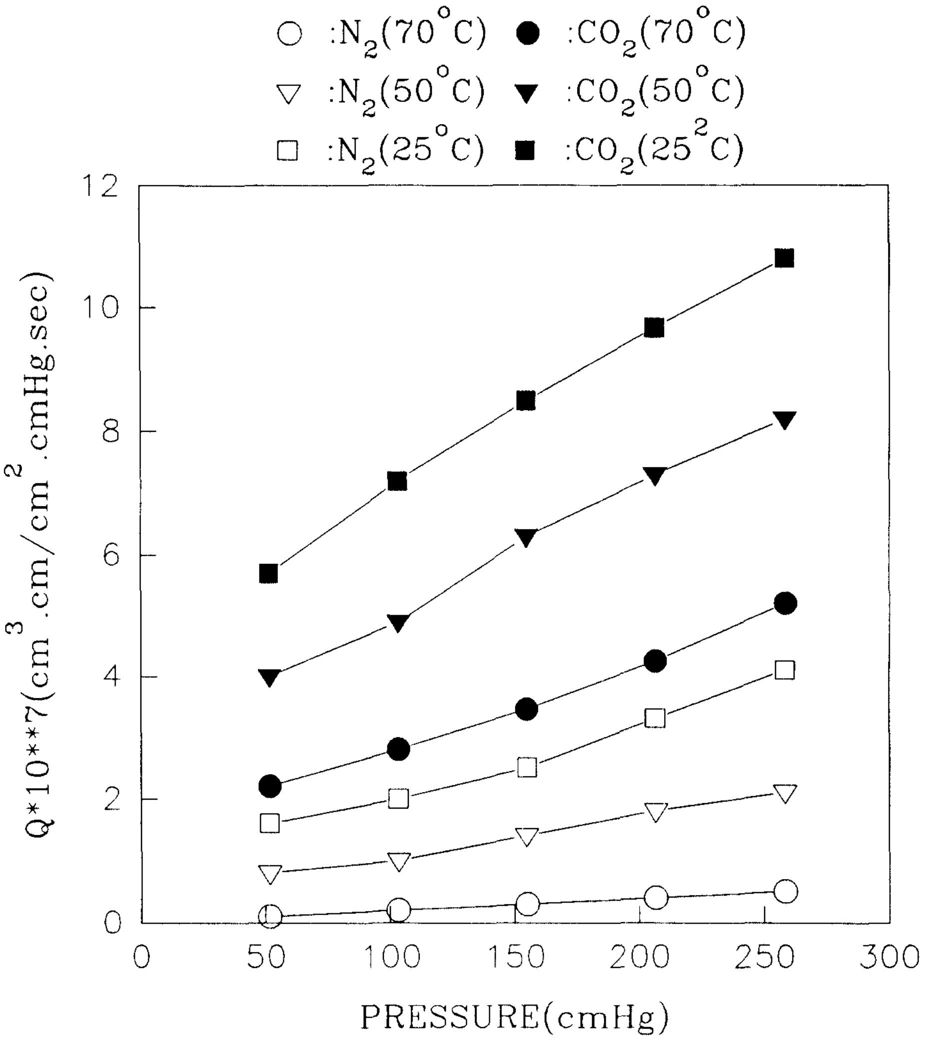

Fig. 2 . Gas permeabilities vs. pressure through the hollow fiber membranes of different temperature. (PEI/GBL/NMP=25/0/75)

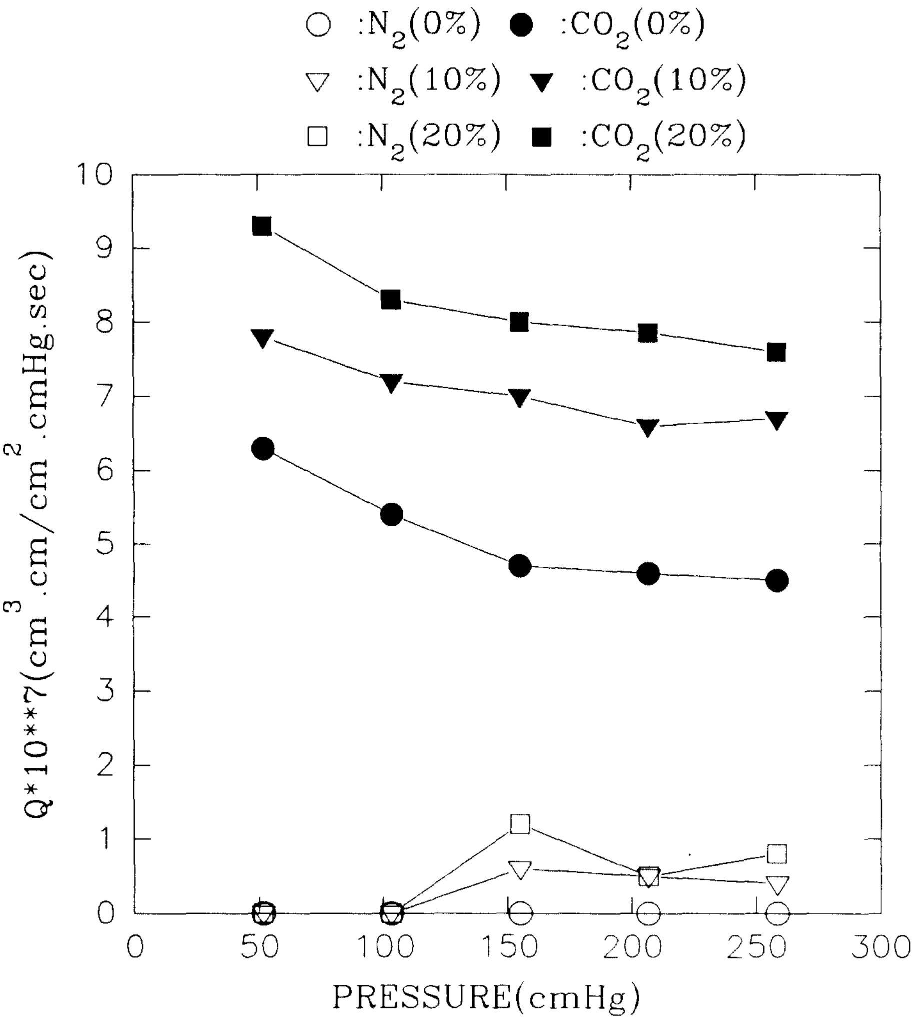

Fig. 3. Gas permeabilities through the hollow fiber membranes containing water vapor in the pores(70°C)

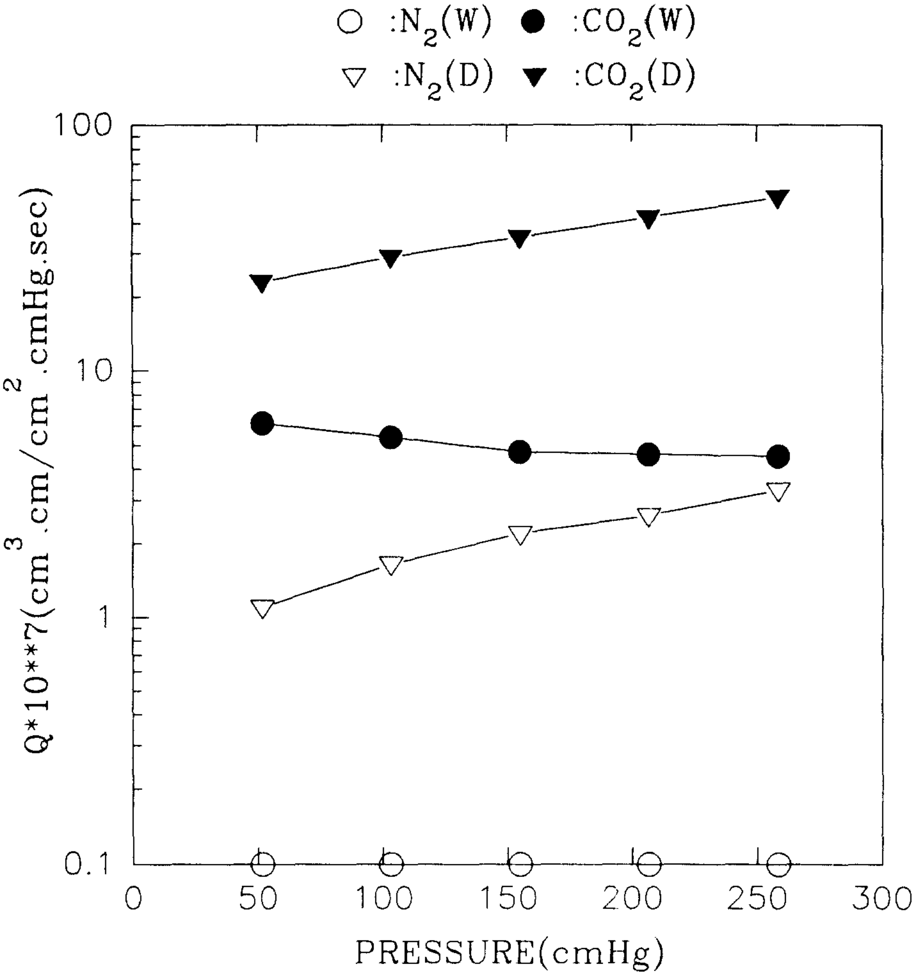

Fig. 4 . Gas permeabilities through the hollow fiber membranes with water vapor(70°C) (PEI/GBL/NMP=25/0/75)

Table 1. The effect of operating condition on the seperation properties of water vapor saturated membranes

Operating condition	ΔP (psi)	Flux ($cm^3/cm^2.cmHg.sec$)	Selectivity
Pressure	20	5.1×10^{-5}	N_2 / CO_2 = 55/45~99.5/0.5
Vacuumⓐ	20	3.0×10^{-6}	22

* Membranes : PEI / GBL / NMP = 25 / 0 / 75
(Saturated with water vapor)
* Feed Gas : N_2 / CO_2 = 80 / 20
* Temperature : 25℃
ⓐ : Upstream : 5 psi
Downstream : Vacuum condition

Table 2. The effect of NaOH treatment on the membranes performance.

Memebranes	ΔP (psi)	Flux ($cm^3/cm^2 \cdot cmHg \cdot sec$)	Selectivity
A	20	3×10^{-6}	22
B	20	2×10^{-7}	87

* Membranes

A : Untreated membrane
B : NaOH treated membrane

* Operating conditions

1. Feed Gas : N_2 / CO_2 = 80 / 20
2. Temperature : 25℃
3. Upstream : 5 psi
   Downstream : Vacuum condition