

PERMEATION OF PURE AND MIXED GASES THROUGH COMPOSITE MEMBRANES PREPARED BY PLASMA POLYMERIZATION OF FLUOROCARBONS

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ABSTRACT

The permeation, solution and diffusion of simple gases (He, H₂, O₂, N₂ and CH₄) and condensable vapors (CO₂, SO₂, C₂H₄ and C₃H₈), and the mixed gases (O₂/N₂ mixtures and CO₂/CH₄ mixtures) through composite membrane was studied. Composite membranes were made by deposition of aromatic fluorocarbons onto polymer substrates of porous Celgard in a microwave discharge.

In the both cases of simple gases and condensable vapors, as the kinetic molecular diameter of the permeant molecules increased, the permeability decreased. However, when the kinetic molecular diameter are similar, the condensable vapors showed higher permeabilities than that of permanent gases.

The vapor solubility increased with increasing critical temperature of the vapors. However, in the case of propane, despite its high critical temperature, it showed lower solubility than other vapors.

The vapor diffusivity decreased with increasing kinetic diameter of the molecule. Compared to conventional polymers, the plasma polymers showed much lower values for vapor diffusivities. The pressure of the permeant did not affect the permeability. The permeability was also not affected by the composition in cases of mixed gases.

I. INTRODUCTION

Recently, the membrane separation technique has been extended to the preparation of composite membranes, in which a dense skin layer and a porous substrate layer are prepared from different polymers. To produce an efficient composite membrane, it is important to make a thin film. With conventional polymers, it is not so easy to make very thin films reliably.

Another way to produce a composite membrane is using the plasma polymerization technique. Plasma polymerization gives ultra thin films with highly crosslinked structure and sub-micron thickness. When the plasma polymer is used for a composite membrane, the crosslinked network structure may give us high permselectivity and the ultra thinness would give us very low permeation resistance. A number of

authors have presented the performances of gas separation plasma polymerized membranes. However, the data were limited to the permeabilities for simple gases—CO₂, CH₄, O₂ and N₂.

The purposes of this work is to extend our data base and our understanding of the permeation properties of plasma polymer-based composite membranes by examining the permeation of gas mixtures, the effect of pressure on the permeability coefficient, and the permselectivity and the permeation characteristics of condensible vapors.

II. EXPERIMENTALS

For the reactor body, a horizontal 34mm I.D. x 40 cm length pyrex glass tube with one sealed end and opened other end was used. For the plasma polymerizations, 2.45 G Hz microwave power was used. The opened end of the tube was connected to a vacuum pump to evacuate the reactor, and between the reactor and the vacuum pump, a throttle valve and a ball valve to control the reactor pressure were installed. The gas and monomers were supplied into the reactor from the external monomer bottle into the reactor. The power was supplied from microwave power generator through power cable, power guide and power circulator into reactor tube. For monomers, aromatic fluorocarbons(PFP, PFT) was used and for substrate, porous Celgard with effective pore diameter of 0.05 μ m and porosity of 38% was used.

In the permeation equipment, one side of a membrane is evacuated under the maximum pressure limit of 10 torrs and is called downstream side. The other side is at a constant pressure between 4 psia and 40 psia and is called upstream side. In the permeation experiment, the pressure difference between upstream side and downstream side is driving force for the permeation. The pressure value in the downstream side was detected by pressure transducer and through the ID converter the pressure signal was transferred to an IBM PC.

III. RESULTS AND DISCUSSION

In both cases of simple gases and condensable vapors, in our plasma polymers, the permeability was mainly dependent on the kinetic

molecular diameter of the permeates as would be expected from the 'molecular sieve' model. However, the model does not accurately account for both permeant gases and condensible vapors at the same time - even though the ethylene has larger molecular size than methane, it showed higher permeability than methane, which is permanent gas. This may be because ethylene has a much higher solubility than methane. Plasma polymer membranes seem to follow an intermediate trend between 'solution-diffusion' and 'molecular sieve' models.

The plasma polymers from fluorocarbon monomers showed very similar values of permeability to conventional fluorocarbon polymer¹.

Like many cases of conventional polymers³, in our plasma polymers, as the critical temperature increased, the solubility also increased in most cases. However, in case of propane, despite its high critical temperature, it showed a very low solubility. That seems to be because the propane molecule has too large size to penetrate into highly crosslinked structure of the plasma polymers.

Generally, it was well known that as the crosslinking density of polymer chains becomes higher^{4,5}, the gas solubility becomes lower. Because the plasma polymers are known to be with highly crosslinked structure, it was supposed that our plasma polymers may show lower values of solubilities than the conventional polymers. However, it was discovered that the solubility values in our plasma polymers were tens of times greater than the values in conventional rubbery polymers. The reason seemed to be because the plasma polymer structure contains lots of free radicals which tends to have interaction with other species.

The diffusivity of gases decreased with increasing kinetic molecular diameter in our plasma polymer. Additionally, just as we have guessed before, C₂H₄ which showed higher permeability than CH₄ showed lower diffusivity. Thus, it became clear that the reason for high permeability was because of its high solubility.

Compared with conventional polymers^{1,2}, the plasma polymers showed much lower values of diffusivity. The reason may be because of highly crosslinked structure of plasma polymer.

In our composite membranes, permeability values were not

dependent on the pressure. From the result, we could see that no swelling effect exists in the very stiff structures of the plasma polymers. Thus, for permeant mixtures, the effect of the composition on the individual permeability coefficients could be expected to be small. In our results for gas mixtures (CO₂/CH₄ mixtures and O₂/N₂ mixtures), the values of permeability and permselectivity were not affected by permeant composition to show 'ideal selectivity'.

To investigate the temperature effect on the gas permeation characteristics, the temperature of the permeation was varied from 35°C to 75°C. In the temperature range, the permeability value followed the Arrhenius equation reasonably. Additionally, the activation energy of permeation increased with the increasing kinetic diameter of permeant gas molecule. When the values of activation energy for permeation in plasma polymers were compared with the values in conventional polymers^{2,6}, because the plasma polymers are known to be with high stiffness of their chains, it could be supposed that the plasma polymers would have higher activation energies than those of conventional polymers. However, the plasma polymer have shown much lower values of the activation energies than conventional polymer. The reason might be because the plasma polymers contain higher ratio of free volume than conventional polymers do. Thus, activation energy of diffusion which is the energy required for gas molecules to pass through the chain structure of polymer membrane would be lowered.

IV. REFERENCES

1. R. A. Pasternak, G. L. Burns, and J. Heller, *Macromol*, 4(4), 470, (1971)
2. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, 50, 413 (1961)
3. Van Aneroogen, *J. Appl. Phys.*, 17, 972 (1946)
4. R. M. Barrer and G. Skirrow, *J. Polym. Sci.* 3, 549 (1948)
5. H. L. Frisch and V. T. Stanneff, *J. Polym. Sci.*, 13, 131 (1954)
6. R. A. Pasternak, J. Christensen and J. Heller, *Macromol*, 3, 366 (1970)