Permeability of Selected Gases Through Radio-Frequency Plasma-Polymerized Films

INTRODUCTION

A fundamental investigation of the gas-phase, vacuum polymerization of vinyl-type monomers under the influence of inductively coupled radiofrequency cold plasma was recently completed.[1,2,3] Characterization of the polymers formed indicated that they were all insoluble and crosslinked. The purposes of this work were to show that adherent plasma-deposited films could be deposited onto a smooth polymer surface and thereby alter the permeability characteristics of the surface.

Linear unplasticized polyethylene membranes of 1-mil thickness were coated with 1–2 microns of polypropylene in a plasma field. An adherent polymer film was deposited which reduced the permeability of selected gases (helium, neon, argon, oxygen, and carbon dioxide) through the membrane.

EXPERIMENTAL

Materials. Linear polyethylene film (Marlex 6003), 1 mil thick, was obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. The infrared spectrum of the film shows that it was unplasticized.

The monomer chosen for plasma polymerization was propylene; gases chosen for permeability measurements were helium, neon, argon, oxygen, and carbon dioxide. All gases were supplied by Matheson Company and were 99.9% pure.

Coating of the Substrate. Samples of the 1-mil polyethylene film were positioned in the plasma reactor and the reactor evacuated to 1×10^{-4} torr, purged with argon three times, and then evacuated again to 1×10^{-4} torr. The reactor was then purged with argon and then the propylene monomer for 1 hr. Then radio-frequency plasma was initiated and the power level adjusted.[2] The pressure of propylene monomer in the reactor was maintained at 0.025 torr. Polymerization was carried out for 24 hr at 10 watts. A 1–2-micron coating of polypropylene was deposited on polyethylene film. After the polymerization was complete, the reactor was bled to atmospheric pressure with argon and the coated film was carefully removed and stored in a desiccator until the permeability measurements were carried out.

Construction of Permeability Measurement Apparatus. The permeability measurements apparatus is shown in Figure 1. It is essentially a Linde-type assembly consisting of a gas inlet from a suitable constant-pressure source, a heat exchanger coil, a Wallace & Tiernan pressure gauge capable of reading inlet pressure up to 500 psig with an accuracy of ±0.5 psig, a permeability cell, and a capillary bubble meter. The rigid connections in the assembly were made of 2.0-mm-I.D. copper tubing. The flexible connections in the assembly were made of 2.0-mm-I.D. nylon tubing, and leak-tight connections were achieved with Swagelok fittings. All valves used in the assembly were Hoke fluid control valves.

The permeability cell assembly was a modified Millipore XX4502500 stainless steel filter. The film was supported by a stainless steel screen placed in the low-pressure side of the cell. The effective surface area of the film for permeation in this cell was 2.84 cm².

The entire permeability measurement assembly was immersed in a constant-temperature water bath maintained at 25 ± 0.05°C by a Haake E51 temperature controller unit. This unit also has a water pump for the circulation of bath water to the capillary bubble meter.

The capillary bubble meter is shown in Figure 2. It consisted of thick-walled, glass capillary tubes 0.5 mm, 1.0 mm, and 1.5 mm in diameter, suitable for measuring low, medium, and high permeation rates, respectively. The lower part of the capillary bubble
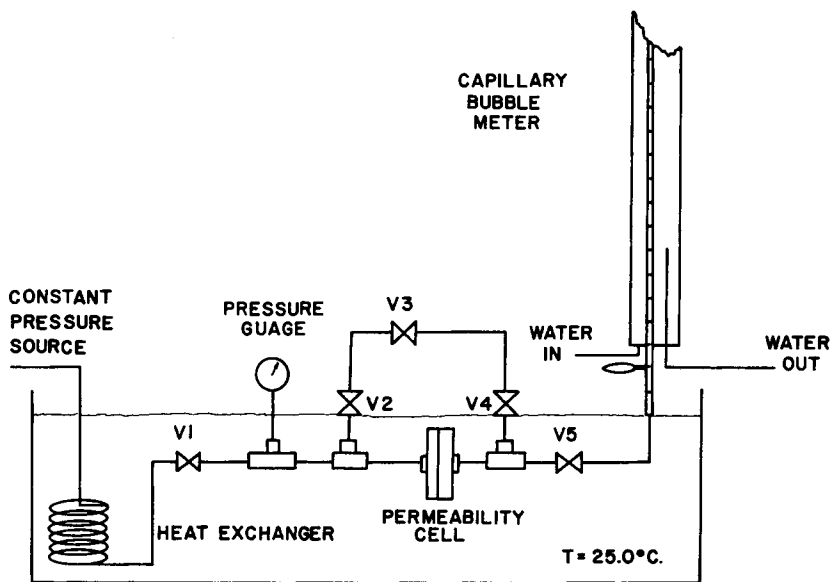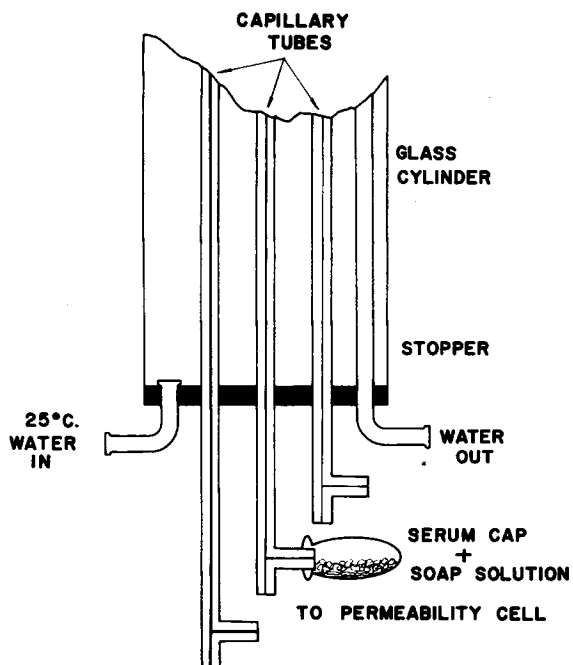
Fig. 1. Permeability measurement apparatus.

Fig. 2. Capillary bubble meter.

meter had two limbs. One limb was connected to a serum cap containing a surfactant solution. The other was connected to the low-pressure side of the permeability cell by means of a Swagelok fitting. In the permeability measurements, the time required for a bubble to permeate a known volume was measured to the nearest second. Each tube was calibrated using mercury at 25°C.

Permeability Measurements. A disc was cut from the uncoated or coated polyethylene film, placed in the cell, and the assembly was made leak tight. The high-pressure side of the cell was thoroughly purged with the gas whose permeability was to be measured. After the system had equilibrated, the time required for a bubble to permeate a known volume of a particular capillary was measured. The measurement was repeated three times for each pressure and the average time was recorded.

The permeability was calculated by means of the equation

$$P = \frac{\Delta Q \times l}{\Delta P \times A \times t}$$

where P = permeability, in cm^3-cm/cm Hg-cm^2-sec; ΔQ = volume permeated at STP, in cm^3; l = thickness of the membrane, in cm; ΔP = pressure drop across the membrane, in cm Hg; A = area of the membrane, in cm^2; and t = time taken for the bubble to permeate a known volume, in sec.

Initially, permeability measurements were made on three 1-mil polyethylene membranes taken at random from three different parts of a film roll. The deviations in the permeability (by least squares) were less than $\pm5\%$. The film was therefore considered essentially homogeneous, with a uniform thickness of 1 mil. The thickness was also measured with a precision micrometer and found to be 1 mil. The permeabilities calculated for He, O_2, and CO_2 through a 1-mil linear polyethylene film were found to agree with those reported by Kammermeyer[4] for the Phillips polyethylene film. The permeability measurements were repeated on a 1-mil polyethylene film coated with 1 to 2-micron polypropylene film.

In order to determine if the plasma itself affected the film properties, a strip of uncoated 1-mil polyethylene film was subjected to radio-frequency plasma for 24 hr at 10 watts in an argon atmosphere. Permeability measurements on this film showed that the plasma field had no effect on the film properties.

RESULTS AND DISCUSSION

The inlet pressure as a function of time is shown in Figure 3 for various gases using both coated and uncoated films. The curves exhibited the same pattern for both coated and uncoated films. In Figure 4, the permeability for each gas is plotted against pressure drop for both the coated and uncoated films. This figure shows that permeabilities for these gases through the film are independent of pressure up to 70 psig.

The permeabilities for He, Ne, Ar, O_2, and CO_2 through uncoated and coated films are tabulated in Table I. When comparing the permeability constants of a particular gas for uncoated and coated films, it is seen that a very thin coating (2 microns) of polypropylene produced by radiofrequency plasma reduces the permeability of the gases considerably.

The permeability constants for each gas through both coated and uncoated membranes are plotted against the square root of the molecular weight of each gas in Figure 5. A close examination of Figure 5 reveals that helium, neon, and argon obey Graham's law for both coated and uncoated polyethylene films. The oxygen and carbon dioxide show a definite dissolution in the uncoated polyethylene film, while in the coated film the membrane appears to be approaching Graham's law behavior. The slight change in slope between helium and neon in the coated and uncoated membranes in Figure 5 indicates that some pores have been either plugged or altered during the coating process.
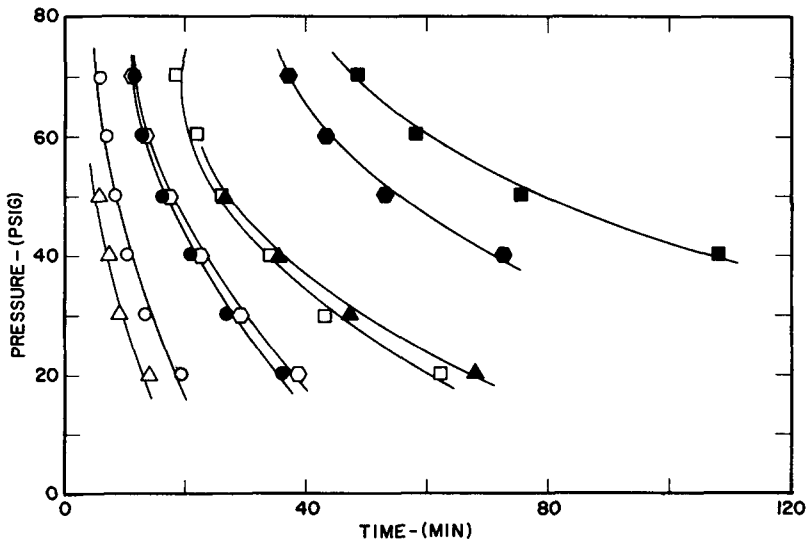
Fig. 3. Inlet pressure vs. time plot. (O) He; (□) Ne; (△) CO₂; (⊘) O₂. Coated film: (●) He; (■) Ne; (▲) CO₂; (⬟) O₂.
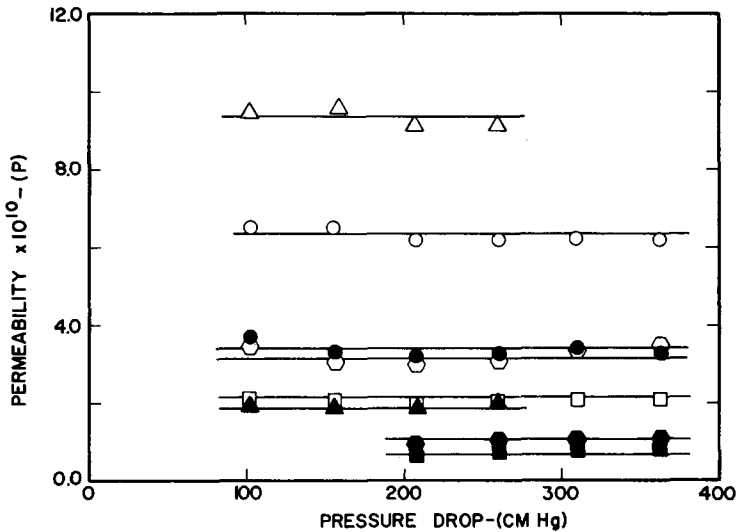
Fig. 4. Permeability vs. pressure drop plot. Symbols are identified in Fig. 3.

Since permeability is the product of the diffusion constant and the solubility constant ($P = D \times S$), both terms must be evaluated. The significant reduction in permeability cannot be explained wholly on the basis of reduction in diffusion through pores. This reduction is due to the fact that the films formed in plasma polymerization are highly crosslinked and exhibit a tight 3D network.[1] (Polypropylene polymers formed in this manner were refluxed in both aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, esters, and ketones for periods up to two weeks without any appreciable change: 1–2% solubility.)

TABLE I
Permeability of Gases Through Uncoated and Coated Films

Gas	Permeability, $\left(\dfrac{cm^3(S.T.P.)\text{-}cm}{cm\ Hg\text{-}cm^2\text{-}sec}\right) \times 10^{10}$	
	Uncoated 1-mil polyethylene film	1-mil Polyethylene film coated with 1–2 microns polypropylene
Helium	6.290	3.33
Neon	2.070	0.72
Oxygen	3.250	1.00
Argon	0.375	—[a]
Carbon dioxide	9.290	1.93

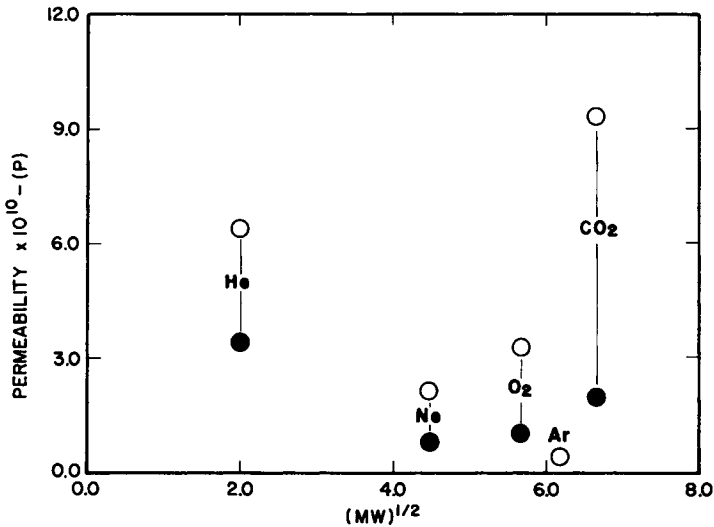[a] Permeation rates were too slow for satisfactory measurements.

Fig. 5. Permeability vs. $(MW)^{1/2}$: (○) uncoated film; (●) coated film.

Thus, in the coated polyethylene film the solubility of the gases O_2 and CO_2 has been reduced and diffusion behavior begins to dominate. The result is a closer approach to Graham's law behavior. It appears possible that by altering the thickness or composition of the coating, Graham's law behavior can be very nearly approached. However, greater film thicknesses could conceivably block all gas flow through the membrane.

CONCLUSIONS

Thin coatings of polypropylene formed in a radio-frequency plasma on polyethylene film are found to reduce the permeability of the gases helium, neon, oxygen, and carbon dioxide. In the case of oxygen and particularly for carbon dioxide, the solubility of the gases is found to be decreased and diffusion behavior seems to be predominant. The diffusion in the coated membrane appears to be approaching Graham's law behavior. This type of behavior could be important in those applications where a definite ratio of

two gases is desired for a particular transfer application or where a specific diffusion rate is required.

References

1. L. F. Thompson, "A Fundamental Investigation of the Gas Phase Polymerization of Vinyl Type Monomers in a Low Power Inductively Coupled 4MHz RF Plasma," Ph.D. Thesis, University of Missouri-Rolla, 1970.
2. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16,** 2291 (1972).
3. L. F. Thompson and K. G. Mayhan, *J. Appl. Polym. Sci.*, **16,** 2317 (1972).
4. K. Kammermeyer, *Ind. Eng. Chem.*, **45,** 1152 (1953).

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