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Testing of Polymer Membranes for the Selective Permeability of Hydrogen[#]

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ABSTRACT

Selective gas barriers are of prime importance in thin polymer membranes. The focus of this work was to find a polymer membrane that allows the transport of H_2 and acts as a barrier to CO_2 and chlorinated organics. Membrane screening has included the following testing: single gas permeability measurements, mixed gas separations, and polymer physical characterization. Single gas permeability measurements were made using the time-lag method for five gases (H_2, O_2, N_2, CO_2, and CH_4). Permeability coefficients and selectivities for the gas pair H_2/CO_2 are presented. Mixed gas separations were performed to measure actual

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separation factors for H_2/CCl_4 and to determine the effects on hydrogen permeability caused by exposing polymers to chlorinated hydrocarbons. The results of basic polymer characterization, such as polymer density and glass transitions, are addressed.

Key Words: Polymer membranes; Gas separations; Hydrogen permeability.

INTRODUCTION

There are many needs for hydrogen separation: fuel cells, recovery of hydrogen for energy production, control of hydrogen for safety concerns, and environmental concerns, such as the reduction of acid gases in emissions from power plants and large industrial factories. One application of very high interest[1] is using polymer membranes as protective coatings for hydrogenation catalysts. In this application, the membrane needs to allow hydrogen to permeate through while excluding potential poisons, such as carbon dioxide and chlorinated organics.

The main focus of this work was to screen a large selection of readily available polymers for hydrogen selectivity. The desired polymers need to fit two criteria: (1) facilitate hydrogen transport at a high enough level to maintain an acceptable hydrogenation rate, and (2) block the permeation of potential catalyst poisons. The polymer screening was carried out in two stages. The first phase was pure gas testing, conducted using the time-lag method.[2–5] The gas permeability measured in the time-lag testing was used to select polymers for the second stage of testing. The second-stage testing included mixed gas testing using a variable volume technique.[6–9] Mixed gas testing determines the actual separation factor for hydrogen over carbon tetrachloride for each candidate polymer. Density measurements were made for each polymer, giving an indication of the diffusive properties of the polymers.

EXPERIMENTAL

Membrane Formation and Thickness Determination

Nonporous, thin, dense film membranes for the single and mixed gas experiments were formed by either solution or melt casting.[9] Finished membranes were mounted on porous ceramic supports with 0.2-μm pore size. Casting solutions were prepared to be 7 to 10% polymer by wt in tetrahydrofuran (THF). Membrane thicknesses were 80 to 120 μm (Mitutoyo caliper ± 2 μm).

Density Determinations

Density determinations for each polymer were made using a displaced helium gas volume apparatus, a Micromeretic Accupyc1300 pycnometer. Polymer samples for density measurements were prepared in the same manner as the membranes used for permeability studies. All density measurements were taken at room temperature.

Pure Gas Testing/Time-Lag Method

The gas testing results were obtained using the time-lag method.[2–5,10] The interactions of the test gases and the polymer membranes were interpreted using the solution–diffusion model. Membranes were exposed to five different individual gases: H_2, N_2, O_2, CH_4, and CO_2, using the apparatus shown schematically in Fig. 1. In a typical experiment, both sides of the membrane are evacuated to an equal vacuum. The test cell is then isolated, and the pressure at zero time is used as the baseline. The feed side is then exposed to the test gas, with the pressure build-up on the permeate side of the membrane being recorded as a function of time. The two quantities that are

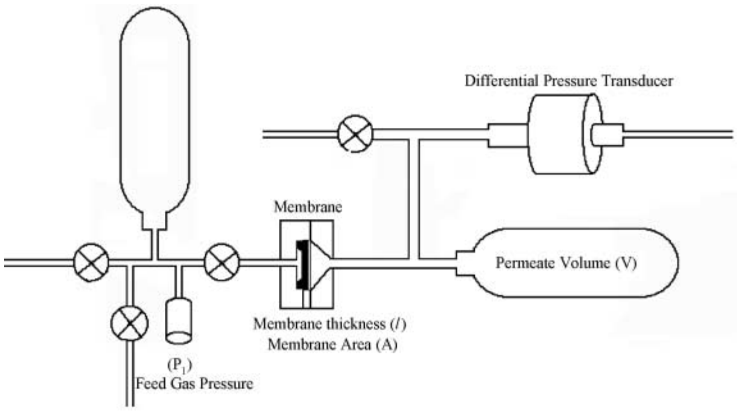

Figure 1. Schematic outline of the pure gas test apparatus.

determined directly from the pure gas test system are time-lag and permeability. The permeability is the rate at which the gas permeates through the membrane after the gas flux has come to equilibrium. The time-lag is the time it takes the gas to permeate from the feed side of the membrane to the permeate side and is used to calculate the diffusivity. The basic relationship of permeability (P), solubility (S), and diffusivity (D) in gas membranes is expressed in eq. (1).

$$P = DS \tag{1}$$

Permeabilities for these experiments were calculated using eq. (2). The test system and membrane variables are as follows: system volume is V (cm^3), the feed gas pressure is p_1 (cm Hg), membrane thickness is l (cm), membrane area is A (cm^2), and T is the system temperature.

$$P = slope \frac{V}{76} \frac{273}{(273 + T)} \frac{1}{A} \frac{l}{p_1} \tag{2}$$

The time-lag, eq. (3), is the intercept of the baseline and the least squares fitted line for the data set after the slope has reached equilibrium. The time-lag is graphically illustrated in Fig. 2. The determined value for the time-lag is used to calculate the diffusivity D [eq. (4)].

$$t = timelag = \frac{baseline - \text{intercept}}{slope} \tag{3}$$

$$D = \frac{l^2}{6t} \tag{4}$$

The solubility is calculated from eq. (1) using the measured permeability and the calculated diffusivity. Time-lag experiments were carried out at constant temperature (30°C) and pressure (30 psi).

Mixed Gas Testing Outline

Mixed gas tests have been carried out to directly measure selectivity.[6–9] As illustrated in Fig. 3, a feed gas is flowed across one side of a membrane at a rate of 4 mL/min. Adjustment between the feed gas regulator and the mass flow controller determine the pressure and feed flow on the membrane. The feed gas pressure for these experiments was 30 psi. Gases that permeate through the membrane are swept away in a nitrogen gas stream. The permeate sweep gas flow is also controlled by a mass flow controller, and is set at

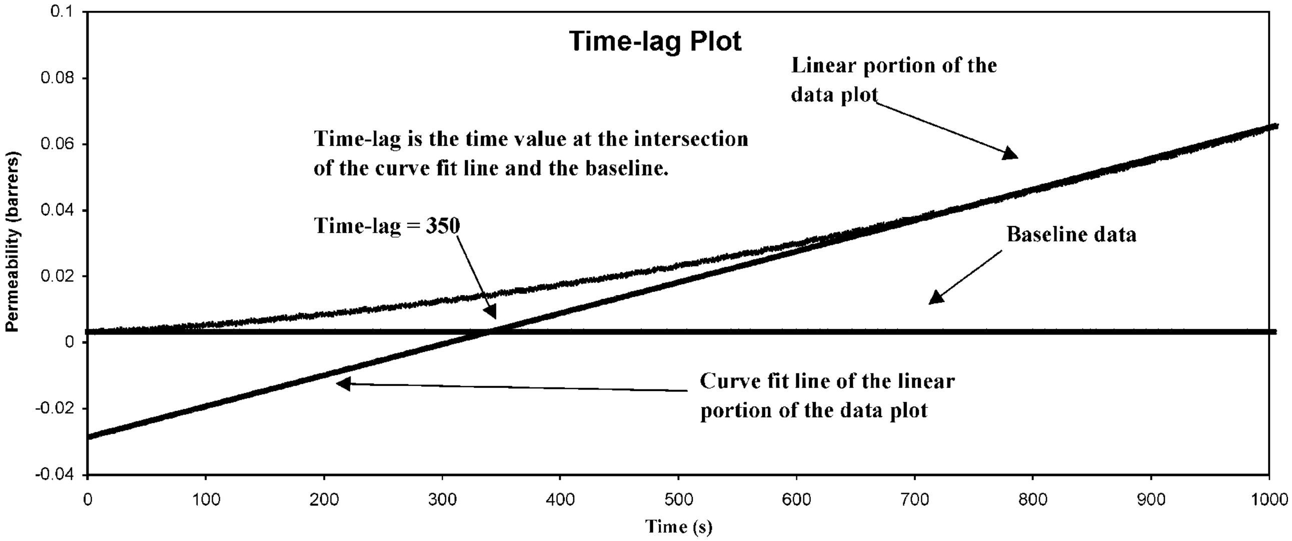

Figure 2. Graphical illustration of time-lag.

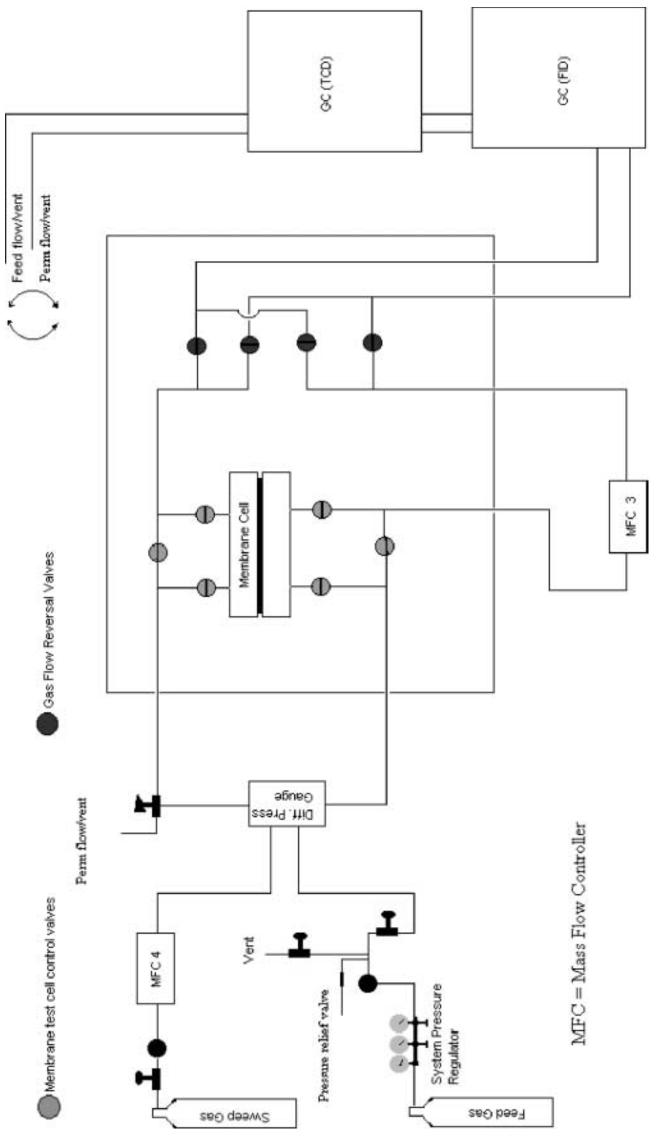

Figure 3. Schematic outline of the mixed gas test system.

2 mL/min. The total permeate flow during testing is measured directly using an electronic soap bubble meter. Both the permeate and feed flows are directed by a series of automated valves through two separate gas chromatographs (GC) equipped with different detectors for analysis. GC A is equipped with flame ionization detectors (FID) for the analysis volatile organics. GC B has thermal conductivity detectors (TCD) for analyzing permanent gases. The test valves and membrane were housed in an oven to maintain a constant temperature of 30°C.

Permeabilities were calculated using eq. (5), where $\Delta V/\Delta t$ is the total flow per unit time through the membrane, $T_{exp}P_{stp}/T_{stp}P_{exp}$ corrects to standard temperature and pressure, *l* is membrane thickness, A is membrane area, and Δp_1 is the pressure differential taken from the feed pressure and concentration determined from the GC analysis.

$$p = \frac{\Delta V}{\Delta t}\frac{T_{\exp}P_{stp}}{P_{\exp}T_{stp}}\frac{l}{A\Delta p_1}. \tag{5}$$

RESULTS AND DISCUSSION

Pure gas permeability measurements were carried out to validate hydrogen permeability in consideration of permeability selectivity over carbon dioxide. For many hydrogen based applications, hydrogen selectivity over compressible gases is of greater concern than overall hydrogen flux.[7–9] The results of the pure gas testing are given in Table 1. Of the polymers screened for these experiments, polystyrene has shown the best combination of permeability and selectivity. Pure gas testing showed that polystyrene, poly(methyl methacrylate), poly(sulfone), and poly(vinylidene fluoride) have ideal selectivities that favor hydrogen over carbon dioxide along with the permeabilities that are promising.

Mixed gas testing was carried out on three separate gas mixtures. Table 2 contains the mixed gas permeability results when the feed gas does not contain chlorinated organics. This feed gas contained only hydrogen (5%) in argon. The mixed gas permeabilities are in relative agreement with the pure gas results. Table 3 contains the results for the initial gas mixture tested in this study that contained chlorinated organics. This feed gas contained hydrogen (5%), methylene chloride (1000 ppm), 1,1,1-trichloroethane (1000 ppm), and carbon tetrachloride (1000 ppm) in a balance of nitrogen. The mixed gas permeability for polystyrene showed an elevated flux over the pure gas result. This may be due to the swelling effect of the chlorinated organics. Kynar and polyethylene show hydrogen fluxes below the detection limit of the mixed gas

Table 1. Pure gas testing results (permeability).

Polymer	H_2 (barrers)	N_2 (barrers)	O_2 (barrers)	CH_4 (barrers)	CO_2 (barrers)	Selectivity H_2/CO_2
Poly(sulfone)	12.1	0.8	1.7	0.4	6.1	2.0
Poly(styrene) MW 280K	23.8	0.6	2.4	0.8	10.4	2.3
Poly(benzyl methacrylate)	11.0	NA	NA	1.4	7.9	1.4
Poly(methyl methacrylate)	2.4	1.2	3.3	0.6	0.6	4
Eval film co-polymer of polyethylene and polyvinyl alcohol	0.5	0.3	0.2	0.2	0.2	2.5
Poly(vinylidene fluoride) kynar	2.4	0.7	1.4	1.3	1.2	2.0
Poly(dimethyl siloxane) PDMS (for reference)	375	299	540	600	1300	0.3
Poly(ethylene) low density film	17.3	4.2	6.3	7.7	17.9	0.9
Poly(vinyl acetate)	15.1	1.3	2.3	0.9	13.1	1.2
Poly(styrene-co-butadiene)	7.9	1.8	0.6	2.5	15.3	0.5

Gas permeabilities were determined under the test conditions of 30°C temperature and 30 psi feed gas pressure.

technique used. This could indicate that one of the three chlorinated organics in the gas mixture is condensing in the polymer, influencing the transport of hydrogen and the other chlorinated organics. Trichloroethane (TCA) gives a very broad undefined peaking in the GC analysis, preventing any meaningful permeability determination. Further investigation is required to conclusively determine if TCA is blocking the hydrogen permeability.

Due to the difficulties in getting reliable hydrogen permeability results when using such a complex gas mixture, testing was also done on more limited gas mixtures. Table 4 contains the mixed gas permeability results when the feed gas contains carbon tetrachloride (1000 ppm) and hydrogen (5%) in

Table 2. Mixed gas permeability for hydrogen (feed gas does not contain any chlorinated organic).

Polymer	Mixed gas permeability (H_2) (barrers)	Selectivity H_2/Ar	Pure gas permeability (H_2) (barrers)	Selectivity H_2/Ar
Poly(styrene)	46.8	—	23	—
Poly(ethylene)	18.8	—	17.3	—
Poly(vinylidene fluoride) kynar	10.9	—	5.7	—
Poly(dimethyl siloxane) PDMS	375	1.25	564	1.14

This gas mixture contains 5% hydrogen in a balance of argon. Permeabilities for this gas mixture were completed at the test conditions of 30°C temperature and 30 psi feed gas pressure.

a balance of nitrogen. The hydrogen permeabilities are comparable to the pure gas results, plus increased carbon tetrachloride permeability could indicate that the carbon tetrachloride is not condensing in the polymer or otherwise influencing the transport of hydrogen. Though the permeability results for hydrogen are in agreement with the pure gas results, the carbon tetrachloride permeabilities are very high in many of the polymers that gave the best results in the pure gas testing. Poly (vinylidene fluoride) has selectivity for carbon tetrachloride over hydrogen of nearly 4, poly (benzyl methacrylate) was 7.3, and polystyrene has showed very high solubility to carbon tetrachloride, with a selectivity of over 1000. The polymer that gave the best results using this gas

Table 3. Mixed gas results (permeability).

Polymer	Hydrogen (barrers)	Methylene chloride (barrers)	Carbon tetrachloride (barrers)
Kynar	NA	15	3
PDMS	395	7205	7461
Polystyrene	299	3	6
Polyethylene	NA	150	140

This gas mixture contains: 5% hydrogen, 1000 ppm carbon tetrachloride, 1000 ppm 1,1,1-trichloroethane, 1000 ppm methylene chloride in nitrogen. Permeabilities for this gas mixture were completed at the test conditions of 30°C temperature and 30 psi feed gas pressure.

Table 4. Mixed gas permeability and selectivity data for hydrogen and carbon tetrachloride.

	Permeability (barrers) H_2	Permeability (barrers) CCl_4	Selectivity H_2/CCl_4	Selectivity CCl_4/H_2
Poly(dimethyl siloxane) PDMS	375–425	10,000–20,000	0.032	31.25
Poly(styrene)	21.4	24,000	0.001	1121.49
Poly(vinylidene fluoride) kynar	2.5	9.4	0.266	3.76
Poly(benzyl methacrylate	2.8	20.5	0.137	7.32
Poly(propylene)	3.5	1.65	2.121	0.47
EVAL film	0.11	1.2	0.092	10.91

This gas mixture contains 5% hydrogen, 1000 ppm carbon tetrachloride, in nitrogen. Permeabilities for this gas mixture were completed at the test conditions of 30°C temperature and 30 psi feed gas pressure.

mixture is polypropylene. Polypropylene shows limited solubility to carbon tetrachloride, with a permeability of 3.5 barrers and a hydrogen selectivity of 1.7 for hydrogen over carbon tetrachloride. The densities of the polymers are needed to explain this data.

Figure 4 shows a plot that correlates density to hydrogen fluxes. The results show a trend for higher hydrogen flux with lower density polymer films. Further work on polymer films cast from a variety of different solvents may give some insight into the effects of the film-forming technique on the density with respect to hydrogen permeability. The relationship between polymer density and hydrogen flux indicates a simple explanation of the mechanism that allows polystyrene to have the highest single gas permeability, as well as good selectivity over the larger, more compressible gases with limited solubility, such as carbon dioxide. Lower density is a good indication of a more open polymer matrix,[11,12] making it more likely to allow smaller diameter gases to pass through more easily. However, even some of the lower density polymers may have very low permeability.[13] The cause of this can be explained by the percentage of crystalline material in a given polymer. A dense, impermeable crystalline area could be thought of as reducing the membrane surface area, thereby reducing the overall permeability of any membrane formed from that polymer.[14–16] With the exception of highly crystalline polymers, polymers with lower densities normally demonstrate the higher gas permeability to small gases like hydrogen. The ideal polymer for the separation of hydrogen from

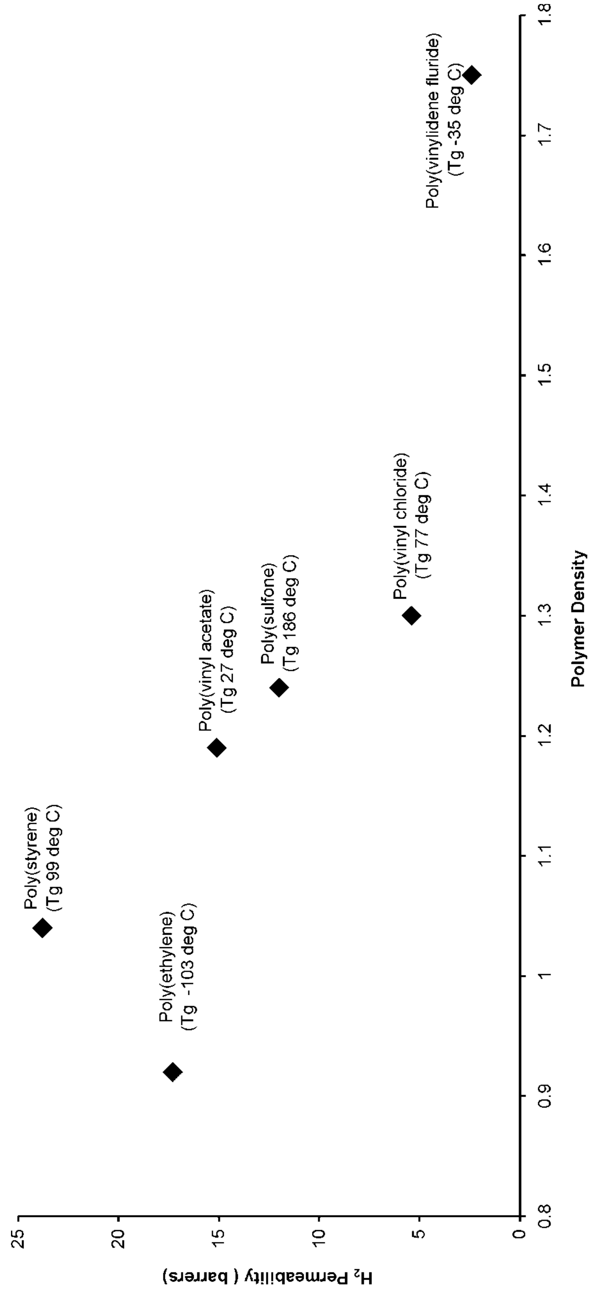

Figure 4. Plot of polymer density against hydrogen permeability.

carbon dioxide or chlorinated hydrocarbons would be a polymer that has an open, highly diffusive matrix while also being very insoluble to the larger, more compressible compounds. The polymers tested in this study may be too soluble in chlorinated organics for use under conditions where the polymer membrane would have prolonged exposure to chlorinated organic compounds. If exposure to these solvents is limited, there could be several applications in waste treatment or in refinery processes where hydrogen could be recovered and utilized in beneficial ways using polymer membranes.[17,18] From the matrix of polymers tested, it seems to hold true that lower density diffusive polymers can allow for the selective transport of hydrogen if the polymer is not highly soluble in the rejectate gas. Polymeric membranes may prove to very useful in gas separation applications that require the separation of smaller diatomic gases from compressible gases or compounds.

CONCLUSION

Hydrogen permeabilities were determined for a number of polymers using the time-lag method. The pure gas testing has shown poly (styrene) to have the best combination of permeability and ideal selectivity of the polymers tested. Mixed gas testing was performed on polystyrene, poly (benzyl methacrylate), poly (vinylidene fluoride), and polypropylene. The mixed gas tests show the hydrogen permeability, for the most part, corresponds well with the single gas permeability. However, the carbon tetrachloride results demonstrate that most of the polymers tested have very high solubility to carbon tetrachloride. Polypropylene was the only polymer tested that shows a favorable selectivity to hydrogen over carbon tetrachloride, due to limited solubility of carbon tetrachloride in polypropylene. The best polymers for the separation of hydrogen from carbon tetrachloride would be polymers that have low density and low solubility to carbon tetrachloride. Density determinations were completed on polymer films that were formed in the same manner as the membranes. A simplistic relationship between polymer density and hydrogen permeability was illustrated. Low density polymers showed a trend for greater hydrogen permeabilities. This work is on going, as we continually search for new polymers with the desired permeability and selectivity properties.

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