CHAPTER IV
RESULTS AND DISCUSSIONS

The rate of transfer for both hydrogen and chlorine through the test materials have to be quantified before identifying an acceptable sheathing material for the sensor. The permeability coefficient of hydrogen and chlorine at evaluated temperature are determined by different standard test methods as discussed in Chapter 3. An acceptable sheathing material is required to have the properties of a high chlorine resistance and a high permeability of hydrogen. It is believed that an acceptable sheathing material should have the ratio of the hydrogen to chlorine permeability coefficients of more than 10 000.

4.1 Determination of Hydrogen Permeability

Potential candidate materials from the previous study were tested to confirm the ability of hydrogen permeation by the standard test method of gas permeation measurement, ASTM F739-91 (1991). The operating conditions were at ambient temperature and evaluated temperatures, using 5% hydrogen gas with argon. The GC Varian 3600 was used as an analytical device.

4.1.1 Teflon Test

A 0.15 mm thick Teflon sample was used to determine the hydrogen permeability for comparison with literature values and the results from the previous study. Numbers shown in Table 4.1 indicate the consistence between the permeability coefficient of hydrogen to 0.15 mm thick Teflon from the experimental and literature values. The permeability coefficient of hydrogen increased with an increase in temperature.

Table 4.1 Permeability coefficient of hydrogen through 0.15mm thick Teflon at ambient temperature and evaluated temperature.

Temperature (°C)	Permeability coefficient (cm^3(STP) cm/cm^2 min atm)	
	Results from present study	Literature value
25	4.50×10^{-6}	4.50×10^{-6} [a]
80	20.78×10^{-6}	-

[a] Goodfellow company catalog 1998-1999

The tendency of hydrogen to permeate through an 0.15 mm thick Teflon sample is shown in Figure 4.1. The average amount of the hydrogen permeation at 25°C and 80°C were 30.75 ppm and 144.98 ppm respectively.

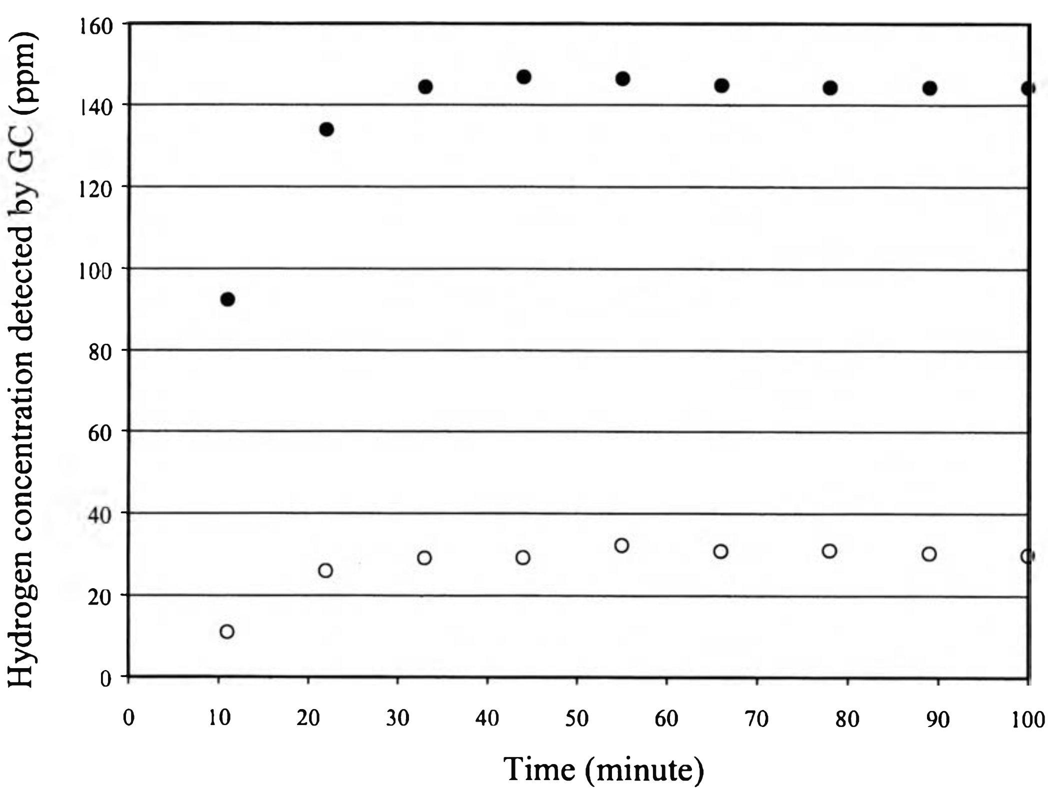

Figure 4.1 Amount of hydrogen permeated through 0.15 mm thick Teflon under steady state condition at ambient temperature (25°C) and evaluated temperature (80°C), o = At 25°C, • = At 80°C.

4.1.2 Material Coatings Test

Different types of materials, Fluorodyn solution, Fluorodyn sheet and Epoxy vinyl ester resin, were coated on the 0.15 mm thick Teflon. The samples were prepared by the coating procedure discussed in Chapter 3. Then the samples were tested at 80°C to determine the permeability coefficient of hydrogen.

a) Fluorodyn Solution Test

Various thickness of Fluorodyn solution were prepared in order to study the relationship between thickness of test material and the value of the permeability coefficient of hydrogen.

Table 4.2 Hydrogen permeability coefficient at 80°C of Fluorodyn solution at various thickness of the coating.

Thickness of Fluorodyn solution coating (mm)	Permeability coefficient of hydrogen$\times 10^{-6}$ (cm^3(STP) cm/cm^2 min atm)
0.07	26.735
0.10	26.890

Table 4.2, gives the value of the permeability coefficient for hydrogen is slightly at two thicknesses. Each thickness represents at least four tests. Figure 4.2 shows the amount of hydrogen from steady state tests that permeated through 0.1 mm thick Fluorodyn solution coating.

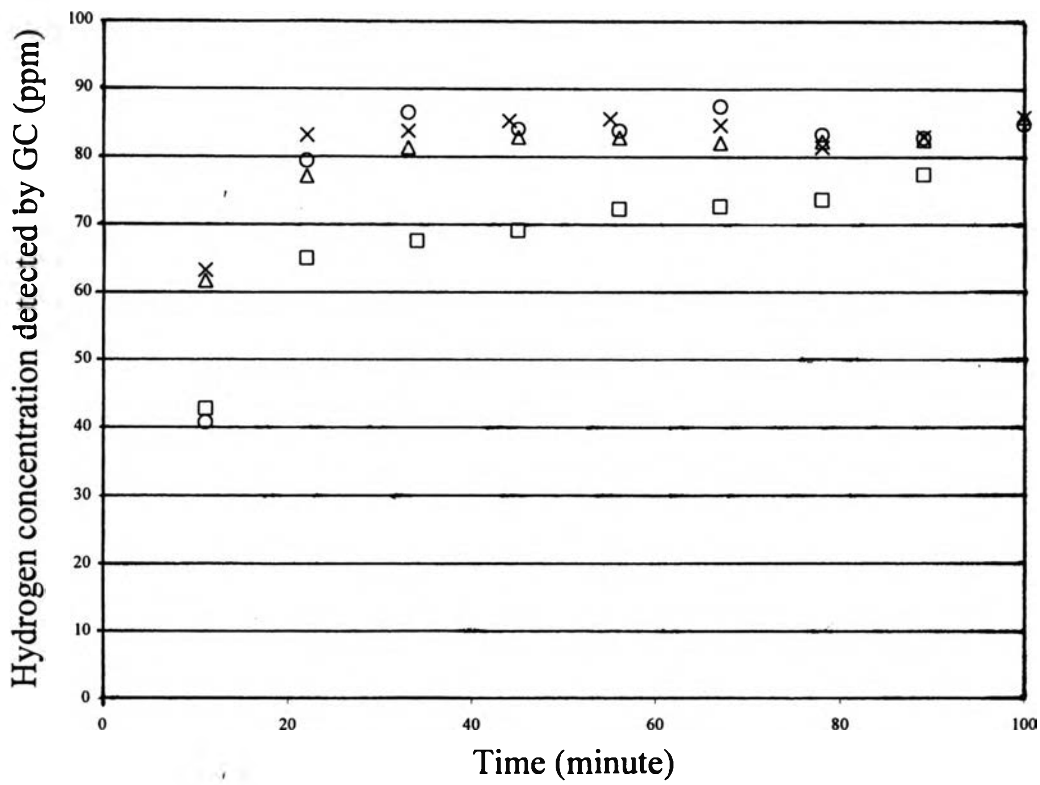

Figure 4.2 Amount of hydrogen permeated through 0.1 mm thick Fluorodyn solution coated on 0.15 mm thick Teflon as a function of time under steady state experiment. Test no.1 to no. 4 were represented by Δ, , o a n d × respectively.

The permeability coefficient of hydrogen to 0.1 mm thick Fluorodyn solution coating was determined as mean value of the amount of hydrogen detected by GC. The average amount of the results showed in Figure 4.2 is 82.33 ppm.

b) Fluorodyn Sheet Test

Fluorodyn sheet of 0.7 mm in thickness was tested with the same procedure as in section 4.1.2.1.

The average amount and the permeability coefficient of hydrogen permeated through 0.7 mm thick Fluorodyn sheet are 39.56 ppm and

26.62×10^{-6} cm^3 (STP) cm/ cm^2 min atm.

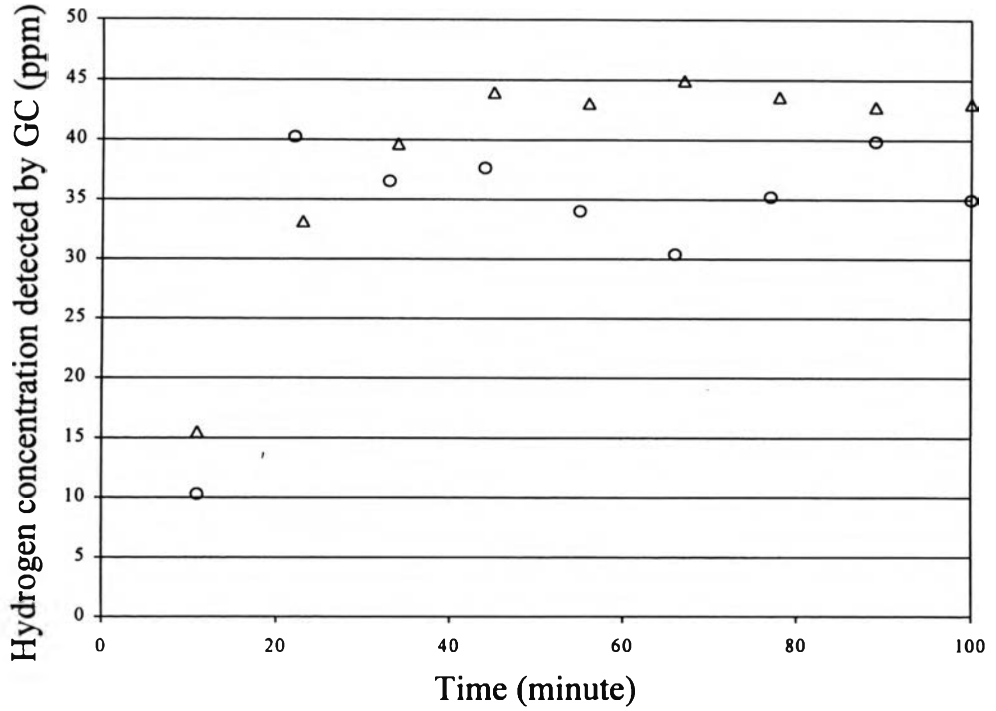

Figure 4.3 Amount of hydrogen permeated through 0.7 mm thick Fluorodyn sheet as a function of time, test no.1 = Δ, test no.2 = o.

c) Epoxy Vinyl Ester Resin Test

Various thickness of epoxy vinyl ester resin were prepared in order to study the relationship between thickness of test material and the value of the permeability coefficient of hydrogen as discussed in section 4.1.2.1 and 4.1.2.2. Table 4.3 shows that the thickness of epoxy vinyl ester resin coating increased from 0.172 mm to 0.900 mm. The value of the permeability coefficients of hydrogen remained the same order of magnitude but decreased with increasing thickness of coating

The permeability coefficient of hydrogen to various thickness of epoxy vinyl ester resin coating was then determined by the average amount of hydrogen detected by GC, for example, the average amount of hydrogen was 32.46 ppm for 0.172 mm thick epoxy vinyl ester resin.

Table 4.3 Hydrogen permeability coefficient of epoxy vinyl ester resin at various thickness of the coating at 80°C.

Thickness of epoxy vinyl ester resin coating (mm)	Permeability coefficient of hydrogen $\times 10^{-6}$ (cm^3(STP) cm/cm^2 min atm)
0.172	7.66
0.230	2.21
0.392	6.31
0.536	1.08
0.900	1.83

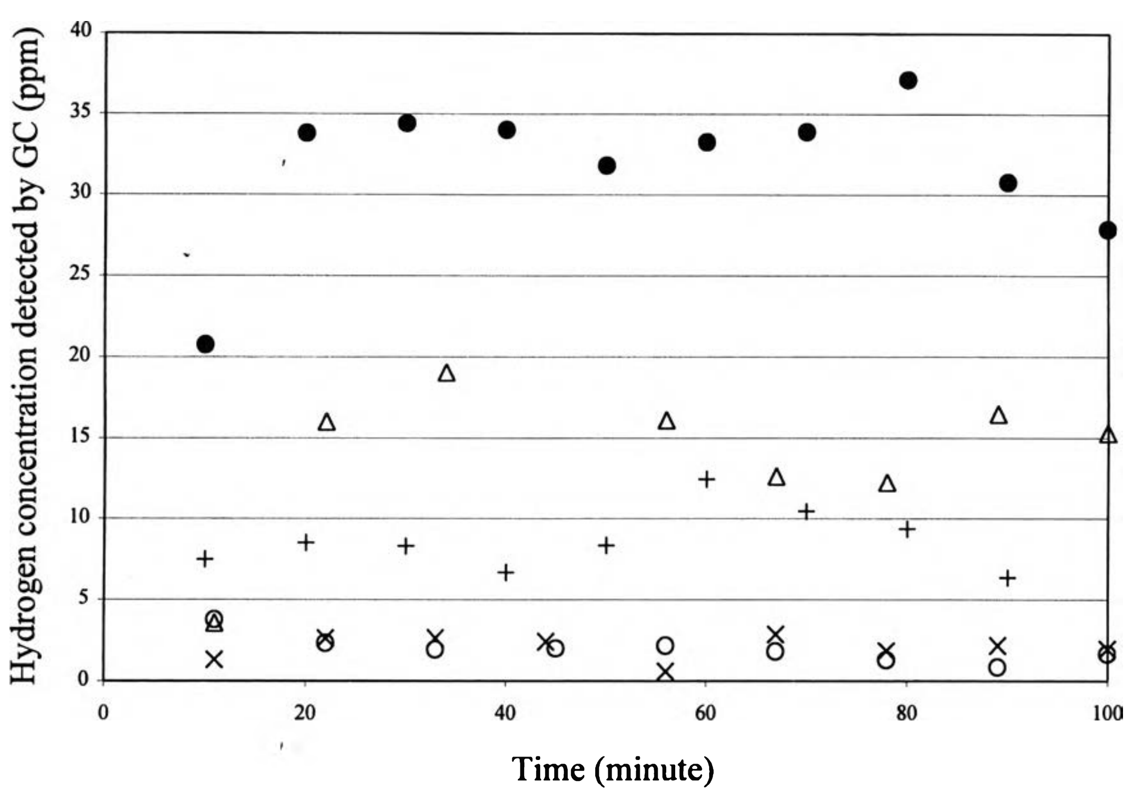

Figure 4.4 Amount of hydrogen permeated through various thickness of epoxy vinyl ester resin coated on 0.15 mm Teflon as a function of time under steady state experiment, • = 0.172 mm, + = 0.230 mm, Δ = 0.392 mm, × = 0.536 mm and o = 0.900 mm.

All the results from the analysis of the hydrogen permeability coefficient determination at 80°C are presented as shown in Table 4.4.

Table 4.4 Effect of an individual property and the thickness of the test material on the permeability coefficient of hydrogen P_{H_2} at 80°C.

Type of coating material	Thickness of material (mm)	Permeability coefficient$\times 10^{-6}$ (cm^3(STP) cm/ cm^2 min atm)
Teflon	0.150	20.780
Fluorodyn solution	0.070	26.735
Fluorodyn solution	0.100	26.890
Fluorodyn sheet	0.700	26.620
Epoxy vinyl ester resin	0.172	7.660
Epoxy vinyl ester resin	0.230	2.210
Epoxy vinyl ester resin	0.392	6.310
Epoxy vinyl ester resin	0.536	1.080
Epoxy vinyl ester resin	0.900	1.830

4.2 Determination of Chlorine Permeability

Test materials that have a potential property of blocking chlorine were tested to determine the permeability coefficient of chlorine using test method indicated by Sarner and Henry (1989). The operating condition was 80°C with dry chlorine gas used as a challenge gas. Argon gas was used as the collection gas. The amount of chlorine which permeated through the test materials was analyzed by Kitagawa precision gas detector tube no. 109SB. In additional, the breakthrough time of chlorine in each material was recorded.

4.2.1 Teflon Test

4.2.1 Teflon Test

0.15 mm thick Teflon sample was tested to determine the permeability coefficient of chlorine. Figure 4.5 shows the relationship between the permeation of chlorine to 0.15 mm thick Teflon as a function of time.

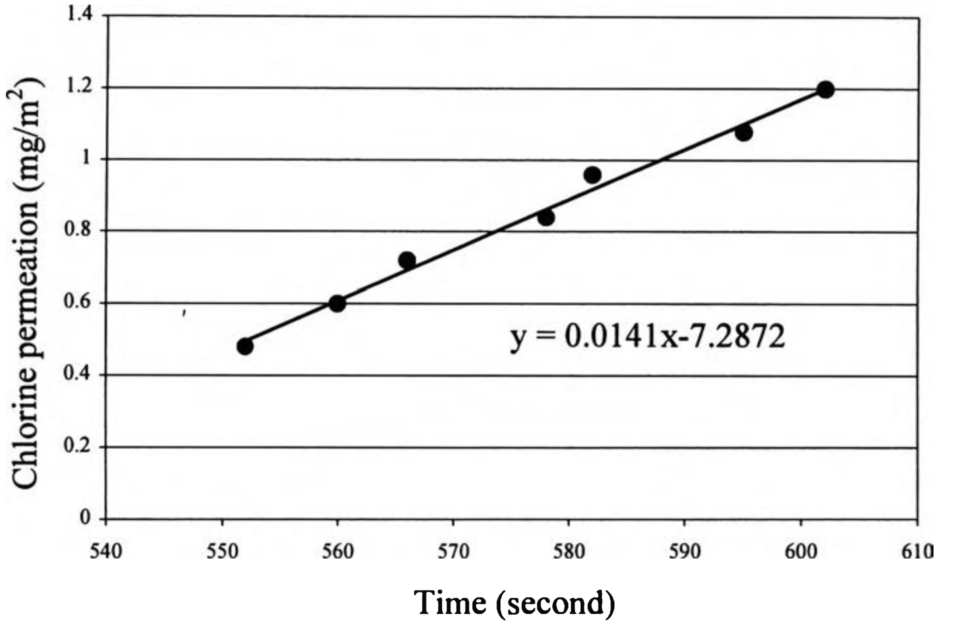

Figure 4.5 The permeation of chlorine to 0.15 mm thick Teflon under steady state condition at 80°C.

The slope of the linear portion, 1.41×10^{-3} mg m^{-2} sec^{-1}, in Figure 4.5 is the permeation rate which is 1.41as stated in section 3.5.1 in Chapter III. The permeation rate of chlorine permeated through 0.15 mm thick Teflon at 80°C is 1.989×10^{-7} mol m^{-2} sec^{-1}.

4.2.2 Material Coatings Test

Different test materials, Fluorodyn solution, Fluorodyn caulk and epoxy vinyl ester resin were coated on 0.15 mm thick Teflon. In addition, 0.7 mm thick Fluorodyn sheet was tested. The samples were used to determine the permeability coefficient of chlorine in each material.

a) Fluorodyn Solution Test

0.41 mm thick Fluorodyn solution was coated on 0.15 mm thick Teflon. The relationship between the permeation of chlorine to 0.41 mm thick Fluorodyn solution coated on 0.15 mm thick Teflon as a function of time was shown in Figure 4.6.

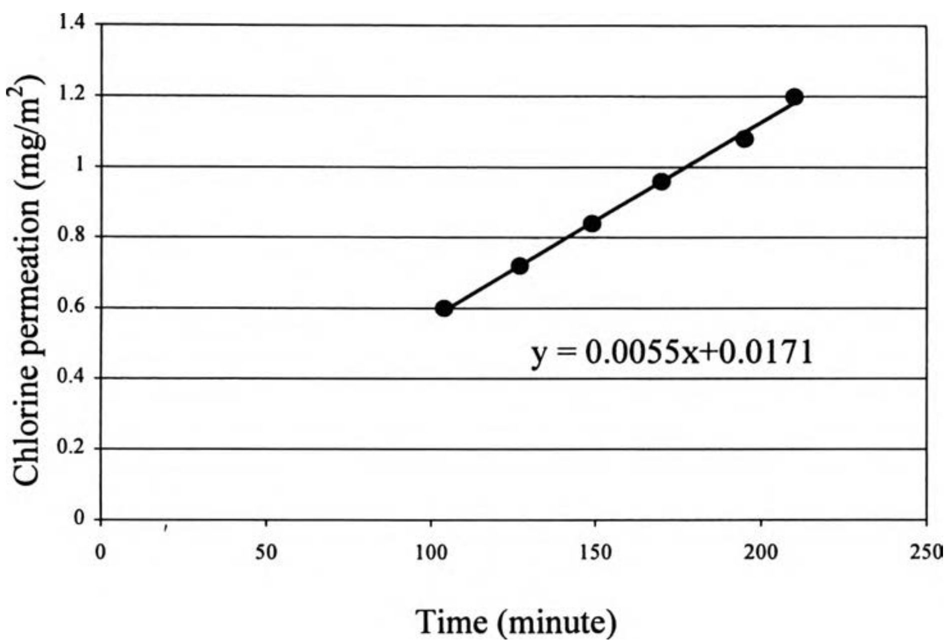

Figure 4.6 The permeation of chlorine to 0.41 mm thick Fluorodyn solution coated on 0.15 mm thick Teflon under steady state condition at 80°C.

The slope of the linear portion showed in Figure 4.6 is 5.5×10^{-3} mg m^{-2} min^{-1} and the permeation rate of chlorine permeated through this sample is 1.293×10^{-3} mol m^{-2} sec^{-1}.

b) Fluorodyn Sheet Test

The 0.7 mm thick Fluorodyn sheet was used as a sample to determine the permeability coefficient of chlorine.

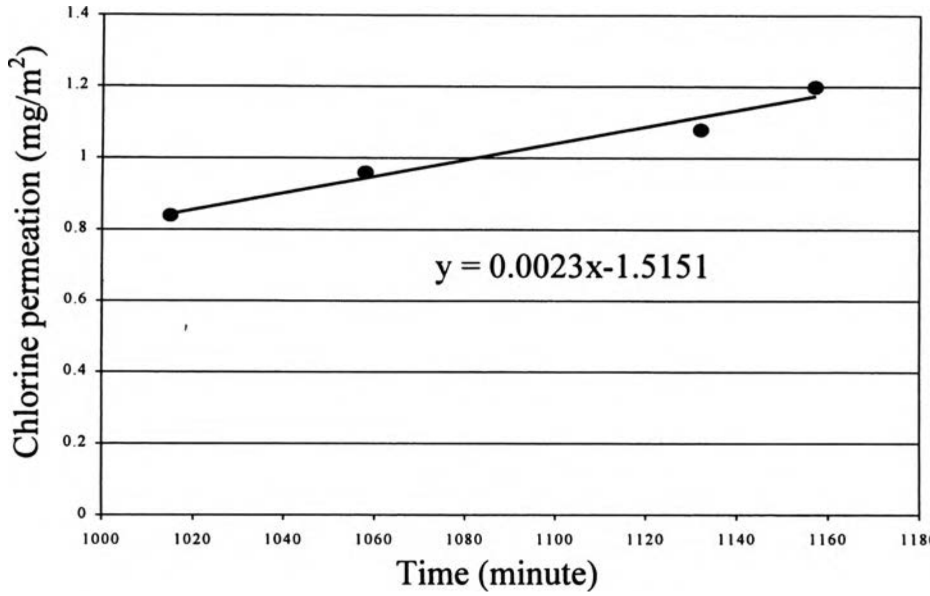

Figure 4.7 The permeation of chlorine to 0.7 mm thick Fluorodyn sheet under steady state condition at 80°C.

From Figure 4.7, the slope of the linear portion showed and the permeation rate are 2.3×10^{-3} mg m^{-2} min^{-1} and 5.406×10^{-10} mol m^{-2} sec^{-1} respectively.

c) Fluorodyn Caulk Test

0.59 mm thick Fluorodyn caulk was coated on 0.15 mm Teflon and tested. The plotted between the chlorine permeation as a function of time is showed in Figure 4.8. The permeation of Figure 4.8 is 1.42×10^{-2} mg m^{-2} min^{-1} and 3.338×10^{-9} mol m^{-2} sec^{-1} respectively.

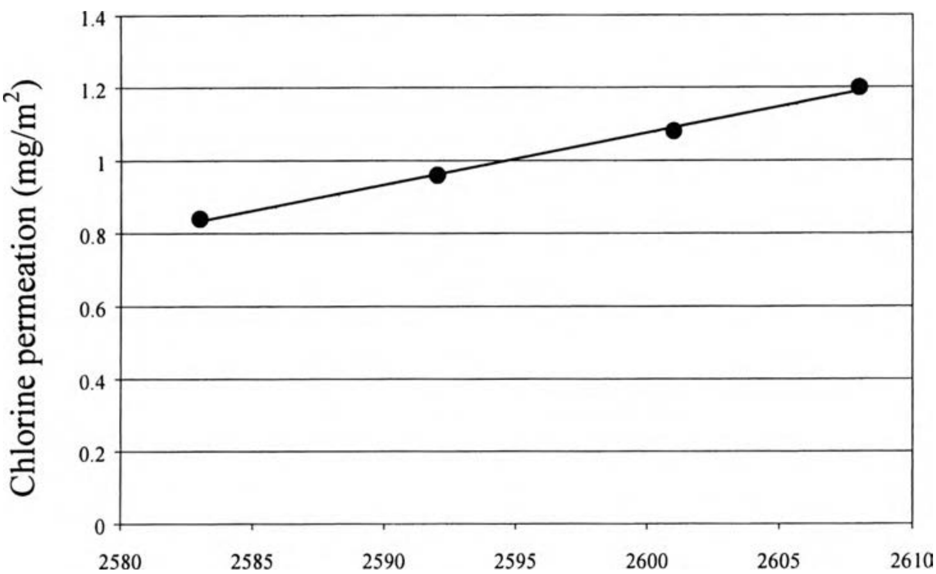

Figure 4.8 The permeation of chlorine to 0.59 mm thick Fluorodyn caulk coated on 0.15 mm thick Teflon under steady state condition at 80°C.

d) Epoxy Vinyl Ester Resin Test

0.54 mm thick epoxy vinyl ester resin was coated on 0.15 mm Teflon and tested with dry chlorine gas as described in section 4.2 and the result is shown in Table 4.5.

Table 4.5 Effect of an individual property and the thickness of the test material on the Breakthrough Time (B/T) and the permeability coefficient of chlorine (P_{Cl2}) at 80°C.

Material	Breakthrough Time (hr)	Permeability coefficient of chlorine (cm^3(STP) cm/ cm^2 min atm)	P_{H_2}/P_{Cl_2} (≈)
0.15 mm Teflon	0.13	4.01×10^{-7}	52
Fluorodyn solution (0.41 mm)	26.67	7.32×10^{-9}	3670

Table 4.5 Effect of an individual property and the thickness of the test material on the Breakthrough Time (B/T) and the permeability coefficient of chlorine (P_{Cl2}) at 80°C. (Cont.)

Material	Breakthrough Time (hr)	Permeability coefficient of chlorine (cm^3(STP) cm/ cm^2 min atm)	P_{H_2}/P_{Cl_2} (≈)
Fluorodyn sheet (0.70 mm)	15.00	5.09×10^{-9}	5230
Fluorodyn caulk (0.59 mm)	39.25	2.69×10^{-8}	1000
Epoxy vinyl ester resin (0.56 mm)	No B/T in 160 hours	-	-

Table 4.5 shows the data for perspective that was used to sheathing material. A ratio of the hydrogen to chlorine permeability coefficients of more than 10 000 was considered desirable. From Table 4.5, the most acceptable sheathing materials among the Fluorodyn materials from the greatest to the smallest ratio are Fluorodyn sheet, Fluorodyn solution and Fluorodyn caulk respectively with no Breakthrough Time in 160 hours for epoxy vinyl ester resin. None of Fluorodyn materials gives a ratio large than 10 000.

4.3 Sample Analysis Using Scanning Electron Microscope

One of the possible defects that could reduce the resistance to chlorine permeation is the presence of pinholes on the coating surfaces. Different types of the test material varied sources of the pinhole. For Example, in the procedure of epoxy vinyl ester resin coating, the bubbles occurred when apply the catalyst, MEKP, on to epoxy vinyl ester resin which was brittle and does not adhere well to the surface. These bubbles could cause the major defect on the protective coating.

Figure 4.9 An example of the pinhole occurred on Fluorodyn solution coated surface from the electron microscope scanner.

Secondly, for the procedure of Fluorodyn coating, the pinhole occurred from the rapid change of the temperature in the oven when curing as shown in Figure 4.9.

The surface of the supported materials in the present study, Teflon was also shown in Figure 4.10.

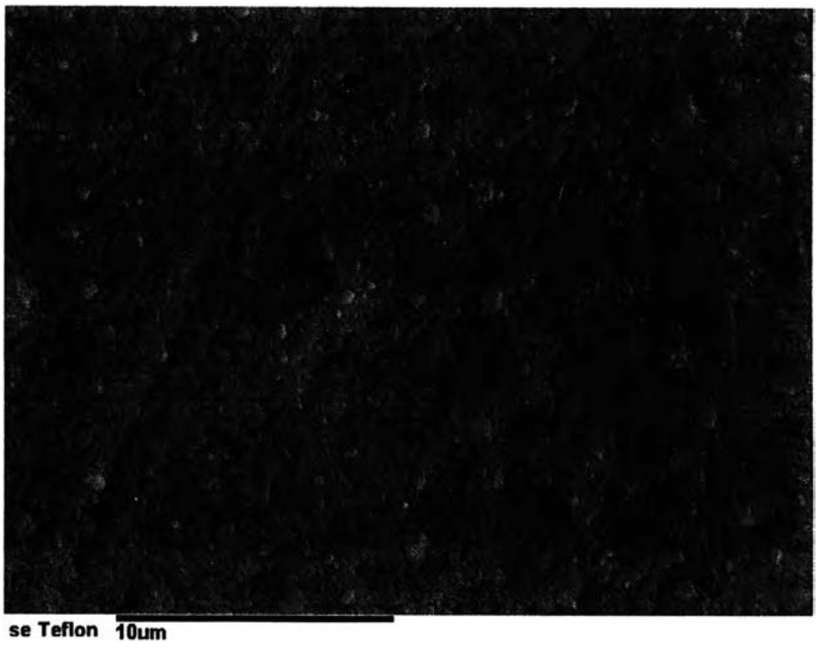

Figure 4.10 An example of Teflon surface from the electron microscope scanner.

The test materials to be used in the gas permeability study should have be homogeneous after being coated on the supported surface as shown in Figure 4.11.

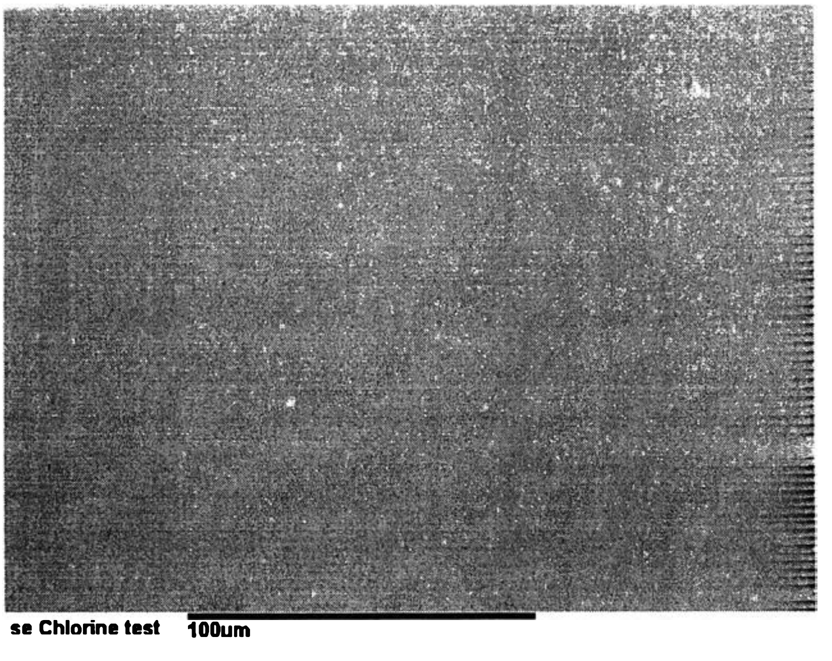

Figure 4.11 An example of a suitable surface of a supported material after being coated that should be used in the gas permeability study.