

Durability of Poly(dimethylsiloxane) When Exposed to Chlorine Gas

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ABSTRACT: Highly crosslinked poly(dimethylsiloxane) (PDMS) is discussed as an alternative membrane material for the gas separation of highly concentrated chlorine gas (90–95 vol %) and oxygen, due to an initial high permeation for Cl₂ and a high selectivity of Cl₂/O₂. It was found that the separation properties of the PDMS membrane change over time upon exposure to aggressive chlorine gas; the flux will go down, and the material may even degrade if not appropriately prepared and protected. The PDMS was exposed to chlorine gas over 4 weeks in a glass chamber at both 30 and 60°C and analysed by (FTIR). The membranes were exposed to chlorine gas in a permeation cell with measurements of the permeability of N₂, O₂, and Cl₂ at regular intervals. The temperature range for the permeation measurements was 30–100°C, and the pressure difference over the membrane was ca. 2 bar. The time of exposure in the permeation cell was several weeks. The absorption of N₂, O₂, and Cl₂ in the PDMS at temperatures in the same range was also measured. This article discusses the durability of the highly crosslinked PDMS membrane following chlorine exposure. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2458–2470, 2002

Key words: poly(dimethylsiloxane); chlorine; degradation; permeability; absorption; Fourier transform infrared

INTRODUCTION

Chlorine is a valuable chemical in very many processes, either as part of the end product or an intermediate product. The unit operations usually involve heavy equipment and liquefaction of the gas where separation is needed; the processes are very energy demanding. The objective for the current investigations was to evaluate the possibility of using membrane separation for purification of

a highly concentrated chlorine gas stream “contaminated” with air during magnesium production. For such an industrial process, the lifetime and stability of the membrane material will be crucial.

The process stream coming from MgCl₂ electrolysis contains mainly Cl₂ (90–95 vol %), the rest being air leaked into the system. The concentration of O₂ has to be reduced to less than 0.2 wt % to avoid any formation of water when H₂ is reacted with Cl₂ to give HCl further down the process stream.¹

The use of membrane processes in chlorine purification is a new approach to gas separation of aggressive gases. Little has been published on this subject. Hägg¹ has documented that poly(dimethylsiloxane) (PDMS) is an interesting

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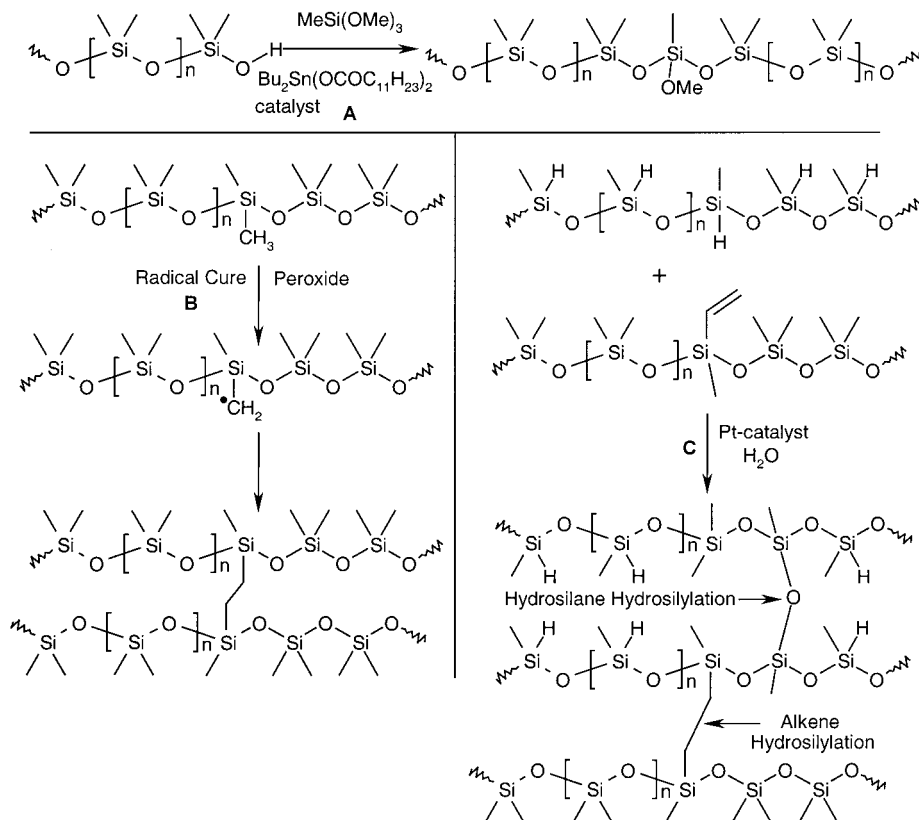


Figure 1 Synthesis for preparing crosslinked silicone membranes.

membrane material for this process due to high permeability for the chlorine gas and a high selectivity for the gas pair Cl_2/O_2 . The problem was, however, to maintain a stable and high flux over time at the temperatures considered ($30\text{--}80^\circ\text{C}$).

Lokhandwala et al.² have published data from a study on recovery of chlorine from chlorine plant tail gas. The tail gas consists of 20% chlorine in 50–70% air, with the balance being hydrogen and carbon dioxide. They found that silicone rubber is stable at low temperatures ($-40\text{--}25^\circ\text{C}$) in the presence of chlorine gas, provided that the membranes are completely crosslinked and have no residual functionality.

The current article gives a discussion on the durability of PDMS materials used for membranes when exposed to highly concentrated chlorine gas at elevated temperatures ($30\text{--}100^\circ\text{C}$) at pressures of 1–2 bar (experimental conditions set by process conditions in Mg production). This involves the evaluation of material properties with regard to structure and transport. Experimental techniques including permeability measurements and absorption measurements have thus been performed, and Fourier transform infrared (FTIR)

analyses have been used to chemically characterize the membrane.

PDMS, with structural formula as given in Figure 1 is a polymer with low glass transition temperature ($T_g = -123^\circ\text{C}$) and low crystallization temperature ($T_c = -40^\circ\text{C}$). The basic properties for PDMS, as stated by Clarson and Semlyen,³ include thermal stability and high permeability to small molecules, organic vapors, and gases with high critical temperatures. PDMS also exhibits properties like low surface tension and a low solubility parameter. Other important characteristics include a high degree of chemical inertness, resistance to weathering, and good dielectric strength. These unusual combinations of properties made PDMS a natural first choice for the separation of Cl_2/O_2 , where Cl_2 would be the fastest permeating component.

THEORY

The origin of many of the properties listed above for PDMS lies in the strength and flexibility of the

siloxane bond, its partial ionic character and the low interactive forces between the methyl groups.³ The siloxane chain is very flexible and bending and torsional movement around the Si–O axis is fairly free, especially with small substituents, e.g., methyl, on the silicon atoms. Rotation is also free about Si–C axis in methyl–silicone compounds. As a result of the freedom of motion, the intermolecular distances between methyl–siloxane chains is greater than between structurally related hydrocarbons, and intermolecular forces are smaller. The small rotational barriers contribute to properties such as low modulus, low glass transition temperature, and high permeability. The general formula implies that the polymer can vary considerably to include linear, branched, and crosslinked structures.⁴ In Figure 1 is shown the synthesis of three different ways for preparing the silicone membranes used in the current study.

Looking at the structural formula, it should be pointed out that exchanging hydrogen for chlorine in the methyl group, or substituting the whole methyl group for chlorine (CCl₃, chlorination) will drastically reduce the freedom of rotation about the Si–O axis and hence change the permeation properties.

Additionally, chlorination can influence cross-linking, which results in changes in the permeation properties and the glass transition temperature (T_g). If the backbone chain is broken, the polymer will degrade and soon produce pinholes in the membrane. All these changes can be detected by exposing the material to the relevant gas (here chlorine) over time and measuring changes in (1) flux, (2) sorption, and (3) by analyzing the changes in structure; these variables will thus provide information about the durability of the membrane material.

The membrane investigated was a composite material with the selective PDMS coated as a dense selective layer on a support made of poly(vinylidene fluoride) (PVDF).

The solution-diffusion mechanism is used to describe gas transport through the dense PDMS membrane. Several steps are involved when a gas or vapour permeates through a polymer membrane: Adsorption and solution of the gas at the interface of the membrane, a sorption process; random movement of the dissolved gas in and through the membrane, a diffusion process; and release of the gas at the opposite interface, a desorption process.⁵

The sorption and desorption are fast, and gas–solution equilibrium is established at the mem-

brane interfaces when constant gas pressures are maintained. In contrast, the diffusion step is very slow, and hence is the rate-determining step in the permeation process.⁵

Fick's law is the simplest description of gas transport through a nonporous structure, i.e.,

$$J_i = -D_i \frac{dc_i}{dx} \quad (1)$$

where J_i is the flow rate through the membrane [$\text{m}^3(\text{STP})/(\text{m}^2 \text{ h})$], D_i is the diffusion coefficient (m^2/h), and the driving force over the membrane, dc_i/dx , is either a concentration gradient [$\text{mol}/(\text{m}^3 \cdot \text{m})$] or for gases (as here) a partial pressure gradient (see below).

The concentrations are related to the partial pressures by Henry's law, which states that a linear relationship exists between the concentration inside the membrane (c_i) (mol/m^3) and the partial pressure of gas outside the membrane (p_i) (bar), i.e.,

$$c_i = S_i p_i \quad (2)$$

where S_i is the solubility coefficient of component i in the membrane [$\text{m}^3(\text{STP})/(\text{m}^3 \text{ bar})$].

The product of the diffusion coefficient D_i and the solubility coefficient S_i is called permeability coefficient P_i [$\text{m}^3(\text{STP})\text{m}/(\text{m}^2 \text{ h bar})$], i.e.,

$$P_i = D_i S_i \quad (3)$$

The combination of eqs. (1)–(3) leads to the familiar expression

$$J_i = -\frac{P_i(p_{o,i} - p_{l,i})}{l} \quad (4)$$

where $p_{o,i}$ is the partial pressure of component i at the high pressure side (bar), $p_{l,i}$ the partial pressure at the low pressure side (bar), and l the membrane thickness (m).

The latter equation shows that the flow rate across the membrane is proportional to the difference in partial pressure and inversely proportional to the membrane thickness.

The overall selectivity of a polymer membrane toward two different penetrant gases A and B is commonly expressed in terms of an "ideal" separation factor, $\alpha^*(A/B)$, which is defined by the relation

Table I Information on the Gases⁸

	N ₂	O ₂	Cl ₂
Molecular weight (g/mol)	28.01	32.00	70.91
Boiling point (°C)	-195.8	-182.96	-34.6
Density (g/L) at 15°C	1.185	1.354	3.042
Critical temperature (K)	126.0	154.6	417.0
Critical pressure (MPa)	3.29	5.043	7.79
Critical density (g/L)	0.519	0.436	0.573
Kinetic diameter L-J (Å)	3.80	3.46	4.22

$$\alpha^*(A/B) = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \quad (5)$$

where the ratios D_A/D_B and S_A/S_B are known as the “diffusivity (or mobility) selectivity” and the “solubility selectivity,” respectively. These ratios represent contributions to the overall selectivity due to the differences in the diffusivities and solubilities of gases A and B in a polymer.⁵⁻⁷

An Arrhenius equation expresses the temperature dependency of the solubility coefficient, S , of noninteracting gases in polymers:

$$S = S_0 \exp(-\Delta H_s/RT) \quad (6)$$

where ΔH_s (J/mol) is the heat of solution and S_0 [$\text{m}^3(\text{STP})/\text{m}^3 \text{ bar}$] is a temperature-independent constant.

For small gases, the heat of solution, ΔH_s , is a small positive value, which indicates that the solubility increases slightly with increasing temperature. For larger molecules, such as nonideal gases like Cl₂, the situation is more complex. Here the heat of sorption is negative and the solubility decreases with increasing temperature.

A similar temperature effect can be observed for the diffusion of gases in the polymer. The diffusion coefficient follows Arrhenius behavior:

$$D = D_0 \exp(-E_d/RT) \quad (7)$$

with E_d being the activation energy for diffusion (J/mol) and D_0 is a temperature-independent constant (m^2/h).

This equation holds for small noninteractive gases, for larger interactive organic vapors, and gases whose dependency is quite complex. For small noninteractive gases the temperature effect of the permeability coefficient is more dependent on the diffusion, since the solubility does not

change so much with temperature. For larger interactive molecules the temperature effect on diffusion and solubility is quite complex, and permeability (P) may decrease with increasing temperature.⁷

From the equations given above, it is seen that information can be obtained about the durability and stability of the material upon exposure to given gases or process conditions by detecting changes in the sorption and flux of a gas through the membrane. The main parameter determining the solubility is the ease of condensation, with molecules becoming more condensable with increasing critical temperature. The critical temperature T_{crit} (K) is a measure of the ease of condensation. Both the critical temperature and the solubility of the gas in the polymer increases as the molecular dimensions increase.⁷ The molecular dimensions and critical temperatures of the gases investigated in the current study are given in Table I. From these data one expects that Cl₂ will permeate much faster than O₂ through a rubbery membrane like PDMS.

Changes in the material upon chlorine exposure are to be expected in the temperature range tested. These changes could result from chlorination, additional crosslinking, or scission of the backbone chain. These mechanisms are all illustrated in Figures 9 and discussed in relation to the results obtained. The changes can be further documented by analyses like Fourier transform infrared (FTIR) or scanning electron microscopy (SEM).

EXPERIMENTAL

Poly(dimethylsiloxane) (PDMS) membranes were prepared in different ways in order to understand the influence of the polymer production process

itself, the curing, and degree of crosslinking on any degradation processes. The PDMS membranes were cured in three different ways: room temperature vulcanization (RTV) [Fig. 1(A)], free radical curing [Fig. 1(B)], and hydrosilylation with a platinum catalyst (note that in the presence of moisture, both disiloxane SiOSi and alkyl Si-CH₂CH₂Si crosslinks can be formed by platinum catalysis) [Fig. 1(C)]. The PDMS prepared by hydrosilylation showed best durability for long time exposure to chlorine gas. The other samples quickly degraded upon exposure even though many of them initially showed high selectivities ($\alpha_{\text{Cl}_2}/\text{O}_2$ up to 30) before they were ruined. The general tendency was that a higher degree of crosslinking was accompanied by a higher degree of selectivity (but lower flux), and such membranes lasted longer than the samples with lower degrees of crosslinking.

The most stable PDMS membrane of all tested was the membrane prepared from hydrosilylation with high degree of crosslinking. The preparation and tests performed with this specific membrane are described in the current section.

Materials

The membranes were cured by hydrosilylation and consist of following starting materials: vinyl-dimethyl-terminated polydimethylsiloxane [$\text{H}_2\text{C}=\text{CHSiMe}_2(\text{OSiMe}_2)_n\text{SiMe}_2\text{CH}=\text{CH}_2$, $M_w \sim 62,700$, $\eta \sim 10,000$ centistokes (Hüls PS445 fluid)]; poly(hydrogenmethyl)siloxane, [(H(CH₃)SiO)_n, Dow Corning DC-1107 fluid]; platinum-divinyltetramethyldisiloxane complex (Gelest SIP 6830.0); hexanes reagent grade (Caledon laboratories).⁹

The vinyl-terminated polydimethylsiloxane (0.425 g, SiCH=CH₂ groups, 1.35×10^{-2} mmol) and poly(hydrogenmethyl)siloxane (0.075 g, SiH groups, 1.2 mmol) were weighed into a beaker and diluted with hexanes (10 mL hexane/g silicone). The polymeric solution was then poured into an aluminum dish or metal mold, followed by the addition of a solution of platinum catalyst (1.5×10^{-4} g catalyst). The dish or mold was covered with a watch glass while evaporation of solvent at room temperature was carried out over 8 h. Curing was then carried out at 80°C for 2 days.⁹

For the absorption measurements, a commercial sample of PDMS elastomer, prepared from a two-component system of 30% silicon product (Dehesive 942) in petrolether, was used. The crosslinking of this standard PDMS was done by

an addition of R₃Si-H groups with platinum catalysis. When preparing the membrane, crosslinking was effected at 30°C; after a specific time, the solvents were evaporated and the resulting films were heated to 80°C for 1 or 2 h to terminate the crosslinking. The membranes for absorption measurements were prepared without support.

As noted, platinum complexes were used as catalysts in the preparation of both materials. It should be noted that residual catalyst might catalyze reactions between the silicone and free chlorine as well as with any HCl present. Further crosslinking at higher temperatures may take place as well.

Permeability Measurements

The permeability flux through the membrane was recorded as increases in pressure (mbar) on the permeate side as a function of time (bar/h), using a MKS Instrument pressure transducer. The data were logged and saved directly into a computer using LabView. The data were then converted in a MatLab program to flux, $J = P/l$ [cm³ (STP)/(cm² cm Hg s)], at given temperature and membrane area.¹

Before a permeability measurement could be performed, the system was evacuated until the pressure was less than 1 mbar (e.g., 0.6 mbar). The system was evacuated overnight prior to starting an experiment, and the evacuation time was at least 1 h between each permeation measurement. The permeabilities of N₂, O₂, and Cl₂ were measured at different temperatures (30–100°C).

The membrane was exposed to Cl₂ by filling the membrane cell with gas and allowing it to stand at the elevated temperature. The total time of exposure ranged from a few days to several weeks, with regular measurements of gas permeability during the exposure time.

Absorption Measurements

A weighed sample of the polymer was placed in a sample cell. The cell was mounted in an insulated temperature-controlled cabinet equipped with MKS Instrument pressure transducers.¹ The volume of the sample cell and connected tubing was carefully calibrated prior to starting the experiment. The exact weight and density of the polymer sample were measured by a pycnometer before it was placed in the sorption chamber. The system was evacuated before the absorption mea-

measurements could start. The evacuation time was recommended to be at least 12 h between each measurement.

New polymer samples were installed for each temperature and the absorptions were measured in the sequence N_2 , O_2 , and Cl_2 . The samples used in the absorption measurements were unsupported.

Sorption was measured by careful registration of the initial pressure in the insulated sorption chamber. The measurement continued until the pressure in the sorption cell was constant ($dp/dt = 0$) and the absorption equilibrium was reached for gas saturation in the polymer sample. The sorbed volume of gas in the sample could be calculated from the reduction in pressure (mbar), either as solubility coefficient, S [$cm^3(STP)/(cm^3 \text{ bar})$], or as sorption level, C [(g gas)/(100 g sample)]. The sorption was measured within the temperature range 25–80°C, and pressure as function of time logged by LabView. The solubility was calculated by using Excel.

Durability Tests in a Glass Chamber

A glass chamber was used to examine the durability of polymers under exposure to chlorine gas over longer time periods. The samples were placed on a glass rack inside the chamber; the chamber was evacuated over night, and then filled with chlorine gas at approximately 1–1.5 bar. The chamber was placed in a temperature-regulated cabinet, and left at 30 or 60°C, for prescribed periods of time (e.g., 4 weeks). For safety, after the exposure and prior to opening, the chamber was carefully evacuated, letting the chlorine gas dissolve in an alkaline liquid (NaOH), and then swept with nitrogen gas. The samples were then analysed by FTIR.

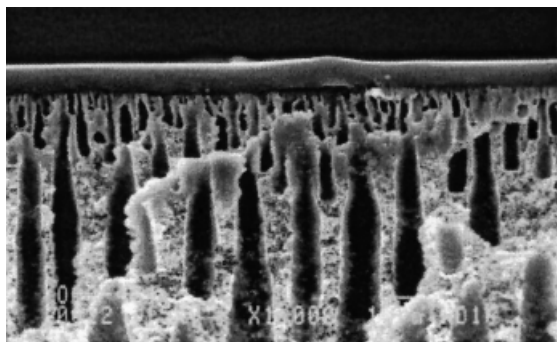


Figure 2 SEM picture of PDMS with high crosslinking for determination of the thickness of the selective layer. Thickness 7 μm .

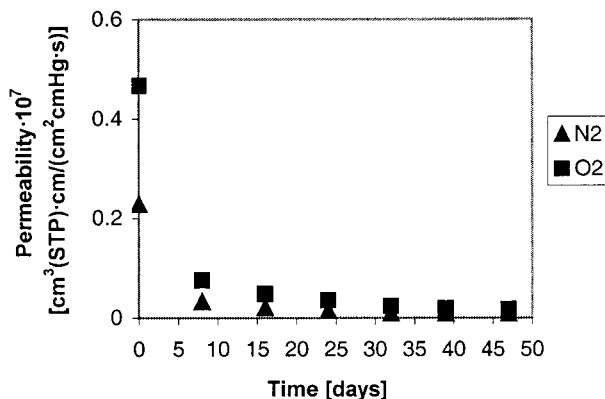


Figure 3 Permeability $\cdot 10^7$ [$cm^3(STP) \text{ cm}/(cm^2 \text{ cmHg s})$] as function of time for N_2 and O_2 in PDMS at 30°C.

RESULTS

Permeability Measurements

Highly crosslinked PDMS membranes were prepared by hydrosilylation using platinum catalysts, exposed to Cl_2 and then examined by permeability measurements.

Permeability measurements were performed at 30°C over a period of 6 weeks. The pressure on the permeate side was 2 bar, while the pressures at the permeate side were about 0.6 mbar. The thickness of the membranes was measured by SEM analysis and found to be 7 μm (Fig. 2). The permeation area, A , was 2.8 cm^2 , hence the permeability, P [$cm^3(STP) \text{ cm}/(cm^2 \text{ s cmHg})$], could be calculated from measured flux, $q = JA$ [see eq. (4)] (m^3/h) at the operating pressure.

Figures 3 and 4 illustrate the changes in permeability for N_2 , O_2 , and Cl_2 in a Cl_2 exposed PDMS membrane (highly crosslinked) as function

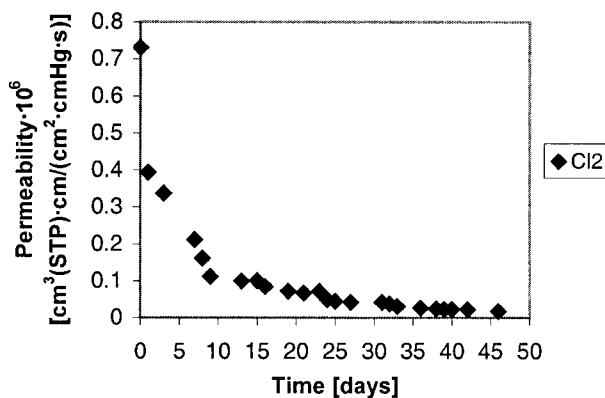


Figure 4 Permeability $\cdot 10^6$ [$cm^3(STP) \text{ cm}/(cm^2 \text{ cmHg s})$] as function of time for Cl_2 in PDMS at 30°C.

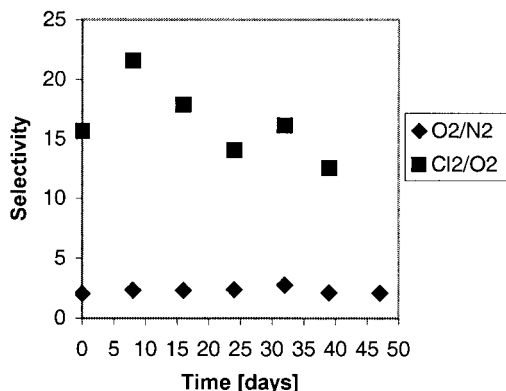


Figure 5 Selectivity of O₂/N₂ and Cl₂/O₂ in PDMS as function of time after exposure of chlorine gas at 30°C.

of time. As can be seen from the figures, the permeability decreased significantly for all three gases during the first week of exposure to chlorine

gas. Changes in the membrane properties were obvious. Over the next weeks the permeability was still decreasing, but to a lesser extent.

The permselectivity for O₂/N₂, given in Figure 5, was constant during the exposure time of 6 weeks, while the permselectivity for Cl₂/O₂ increased during the first week of exposure and was decreasing thereafter. An 80% decrease in the permeability for both chlorine and oxygen during the first week of exposure could be observed. During the second week of exposure a ca. 40% decrease in permeability for both chlorine and oxygen was registered. The material has obviously gone through its main changes during the first week of exposure, and a “new” membrane material was formed. The changes in the material led to changes in the diffusion and solution parameters, which thus contributed to changes in selectivity.

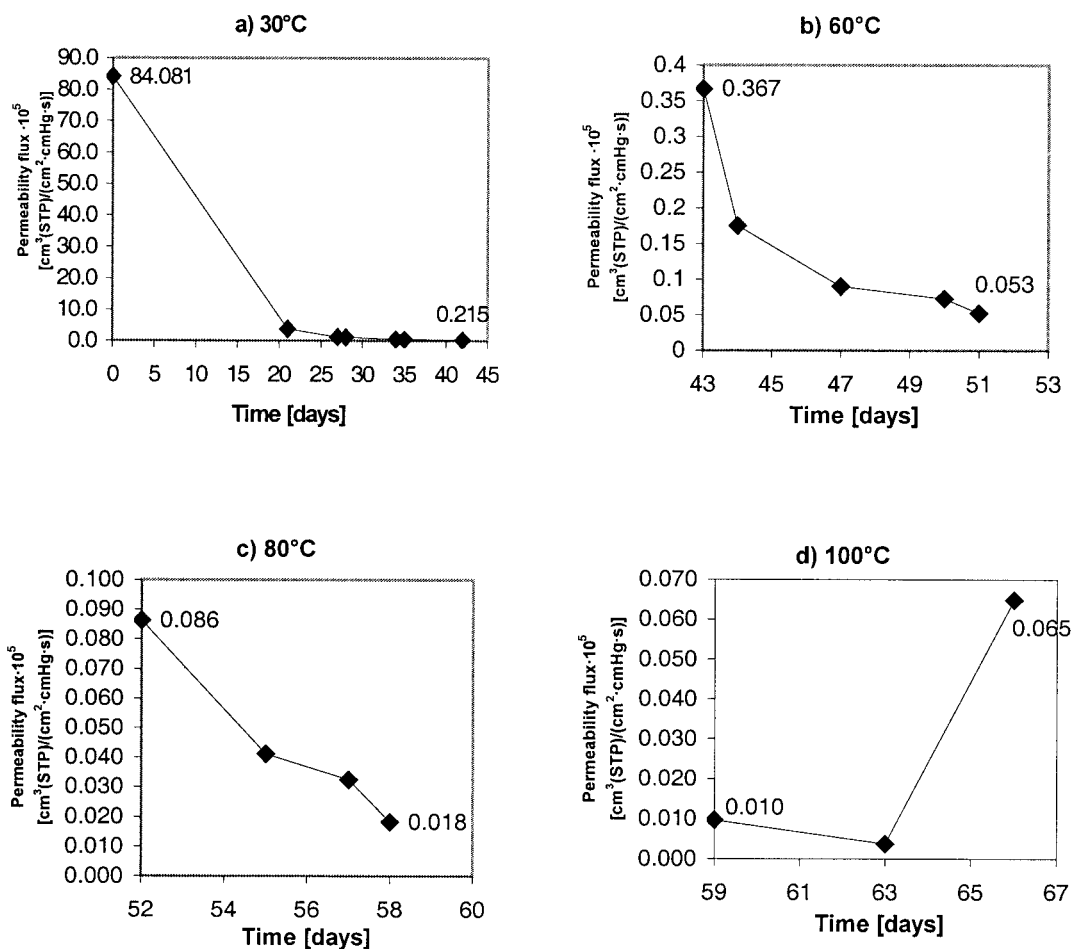


Figure 6 Permeation flux · 10⁵ [cm³/(cm² cm Hg s)] of Cl₂ at increasing temperatures: (a) 30°C, (b) 60°C, (c) 80°C, and (d) 100°C.

Table II Solubilities in standard PDMS.¹

Temp. (°C)	Solubility coefficient, S , [$\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ bar})$]				
	H_2 2 bar	N_2 2 bar	O_2 2 bar	Cl_2^{a} 1 bar	Cl_2^{a} 3 bar
25	0.191	0.220	0.314	10.22	13.29
35	0.193	0.222	0.316	8.22	11.10
50	0.197	0.225	0.320	7.60	8.97
65	0.195	0.230	0.325	6.63	7.29
80	—	—	—	10.1	5.00

^a The measured data have been corrected according to compressibility (factor z).

Figure 6 (a–d) shows the changes in permeability flux (P/l) over time within the temperature range 30–100°C of a sample with unknown thickness.

An increase of temperature clearly speeds up the reactions, causing changes in the material and resulting in a decreased permeation flux for the chlorine gas (note the scale for permeability flux on each figure). The sudden increase in permeability at 100°C accompanied the degradation of the membrane, probably caused by pinholes or cracks in the selective layer. This was confirmed when opening the permeation cell: The membrane had become brittle.

The selectivity of Cl_2/O_2 at the start of the experiment was 17.5 but decreased to 13.6 during 6 weeks of exposure to chlorine gas at 30°C. After 1 week of exposure to chlorine gas at 60°C, the Cl_2/O_2 selectivity had decreased to 5.0.

Absorption Measurements

The measured sorptions of H_2 , N_2 , O_2 , and Cl_2 in PDMS samples are shown in Table II. There was a slight increase in the sorption of hydrogen, nitrogen, and oxygen with increased temperature. The sorption of chlorine decreases with increasing temperature.

An Arrhenius plot of the solubility coefficient, following eq. (6), can be drawn to find the heat of solution (ΔH_s , Fig. 7 and Table III). The heat of solution, which contains both a heat of mixing term and a heat of condensation, can be either positive (endothermic) or negative (exothermic). For the small molecules H_2 , O_2 , and N_2 , ΔH_s is found to be positive in agreement with theory, and indicates the solubility increases with increasing temperature. By contrast, the sorption for chlorine decreased (Table II).

Density

The density of the PDMS was measured with a Multipycnometer after each absorption measurement. The results are given in Table IV. The density before exposure to chlorine gas was ca. 1.08 g/cm^3 . The density increased with the exposure temperature until 65°C. At 80°C, the density had decreased relative to 65°C. The increase in density was most likely due to further crosslink-

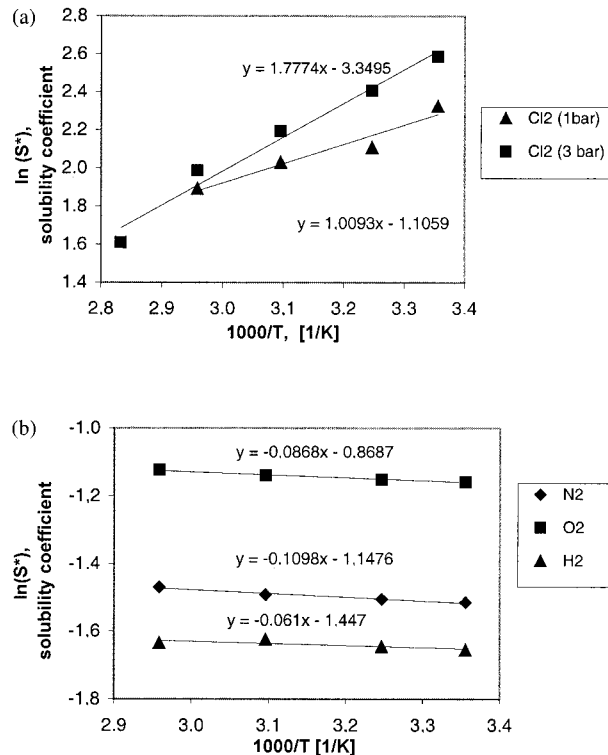


Figure 7 Arrhenius plots of solubility coefficients S^* ; [$\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ bar})$] in PDMS: (a) Cl_2 shown for both 1 and 3 bar and (b) H_2 , N_2 , and O_2 for pressure 2 bar.

Table III Heat of Solution (ΔH_s) in PDMS

	S_o	ΔH_s (kJ/mole)	Regression R^2
H ₂	0.24	0.56	0.63
N ₂	0.32	0.91	0.97
O ₂	0.42	0.72	0.98
Cl ₂ (1 bar)	0.33	-8.9	0.94
Cl ₂ (3 bar)	0.035	-12	0.98

ing and stiffness in the polymer chains caused by chlorine. The decrease at 80°C may be due to degradation of the polymer.

FTIR Analysis

The highly crosslinked PDMS was exposed to Cl₂ in a glass chamber for 4 weeks at both 30 and 60°C. The sample exposed to chlorine gas at 60°C became brittle and cracked easily. The surface had clearly changed during exposure, as indicated by the change from glossy to dull. The samples were analyzed for changes in the material from exposure to chlorine by FTIR.

Figure 8 shows the FTIR spectra of the unexposed and the exposed membrane samples. The analysis was performed with Horizontal Attenuated Total Reflectance (HATR) with a ZnSe crystal, which has a transmission range between 17,000 and 650 cm⁻¹.

A band at 2962 cm⁻¹ indicating the CH₃ stretching vibration was observed in the spectra of the unexposed samples, but had disappeared in the spectra of exposed samples. The band at around 1400 cm⁻¹ was due to the asymmetric CH₃ deformation. Si-CH₃ was characterized by a very strong sharp band at band at 1258 cm⁻¹ in the samples due to CH₃ symmetric deformation. The methyl groups in PDMS had bending absorptions at 840–795 cm⁻¹. PDMS was trimethylsilyl-terminated and the absorption band at 840 cm⁻¹ may indicate these groups, although the length of the siloxane polymer chain will dilute the effect. The band at 880 cm⁻¹ is due to either Si-H or, more likely, to Si-OH stretching vibration. The band at 1178 cm⁻¹ could be due to some C-F bond related to the support structure PVDF.¹⁰

Comparing spectra for unexposed and exposed samples at 30°C, the main difference is the almost complete disappearance of the bending absorption at 795 cm⁻¹; the methyl groups have obviously changed character. The occurrence of bond

731 cm⁻¹ is consistent with formation of a C-Cl bond by chlorination of the methyl group connected to the silicon atom.

After further exposure to chlorine, the 731 cm⁻¹ peak is lost, consistent with the oxidative cleavage of this group. The Si-O-Si band has also changed character in the spectra. Since cyclic tetramers and pentamers have absorptions near 1090 cm⁻¹, it may indicate a depolymerization of the main chain and cyclic compounds or, more likely, that crosslinking has occurred.

The Si-Cl group absorbs at 625–420 cm⁻¹ and possible formation of this bond is therefore not confirmed here since the transmission range for the crystal used in FTIR analysis only goes down to 650 cm⁻¹.

Problems with Impurities

The material degraded very quickly when placed directly on a metallic sinter in the membrane cell. The cell metal (Fe) reacted with the chlorine gas to give iron halide. This product is a Lewis acid and is known to catalyze a degradation of the polymer by depolymerization. This reaction product could further catalyze oxidative modification of the methyl groups and enhance degradation of the membrane material (see below). Thus, care must be taken to avoid direct contact between the membrane material and the steel in the membrane cell used. Teflon sinters and Teflon filters were used, therefore, to protect the membrane material from contact with steel. In the absorption cell, a small glass cylinder was used for the protection of the polymer material. Similarly, the long-term exposure chamber was made out of glass to obviate membrane/steel contact.

Rinsing the composite membrane in water was part of the production process. It is very important to ensure that no particles are trapped in the membrane during this operation: These spots may later be propagation sites for degradation in

Table IV Density of PDMS After Exposure to Cl₂ at Different Temperatures

Exposure Temp. (°C)	Density Measured at 20°C (g/cm ³)
30	1.14
35	1.18
50	1.22
65	1.23
80	1.16

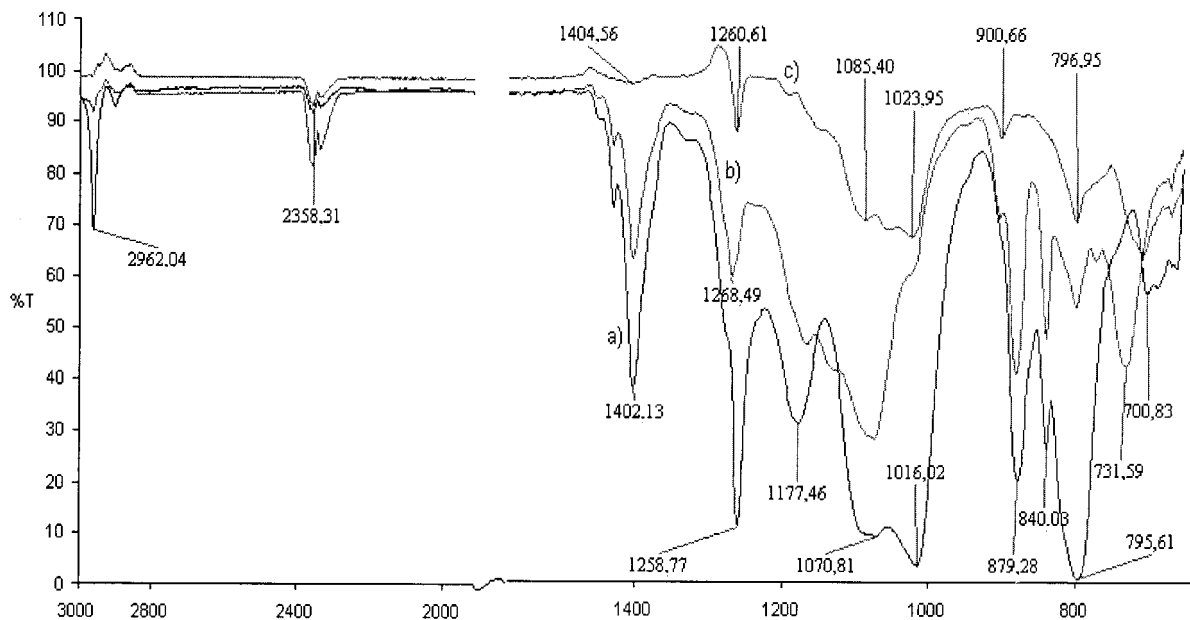


Figure 8 FTIR spectra of PDMS: (a) unexposed sample, (b) exposed at 30°C, and (c) exposed to 60°C.

presence of chlorine gas. From observations under microscope, chemical erosion of this type seemed to be particularly problematic at the junction between the support material PVDF and the PDMS. Deionized, ultra pure water should possibly be used instead in the future.

DISCUSSION

Permeation in silicone membranes will be dramatically affected by chemical changes taking place in the active layer. However, the actual affect on selectivity and flux will depend on the exact chemical reactions. We first describe the major chemical reactions that can occur in these systems and then relate the temporal dependence of membrane performance to silicone structure.

Chlorination of the methyl groups on silicones, a free-radical substitution process, changes both the character of the silicone and produces important catalyst by-products. As shown in Figure 9 (A,B) the process leads sequentially to bulkier side groups with the result of less flexibility of rotation around the main chain. Such changes are expected, based on the properties of other silicones with nonmethyl side chains, to have higher values of T_g (the T_g was, however, not measured

after the exposure to chlorine). An increase in T_g is also expected to result from the greater polarity of these chlorine-modified silicones.

Crosslinking in these polymers can occur by a variety of processes. The chlorination noted above, in the presence of oxygen, can generate carbon radicals. These, as in high temperature vulcanization, can lead to crosslinks via two carbon bridges [Fig. 9(C,D)]. Further oxidation of these activated carbons generates trifunctional silane units [Fig. 9(E)]. Alternatively, such groups may be obtained from residual Si-H groups on the polymer chain either by reaction with chlorine or HCl [Fig. 9(F)].¹¹ Moisture will lead to silicone crosslinking of such polymers irrespective of their source [Fig. 9(G)].¹¹

Depolymerization of the silicone is catalyzed by HCl and by Lewis acids, such as the metal halides, including FeCl₃, produced by the chlorination of steel.³ These depolymerization processes are accompanied by the formation of silicone cyclics that may be lost by evaporation or swell the polymer.

It is necessary to emphasize that the membrane must be totally protected from contact with humidity, particles, and steel since all these factors catalyze degradation. Caution must also be taken when preparing the polymer to avoid hydroxyl-terminated polymer chains. Hydroxyl re-

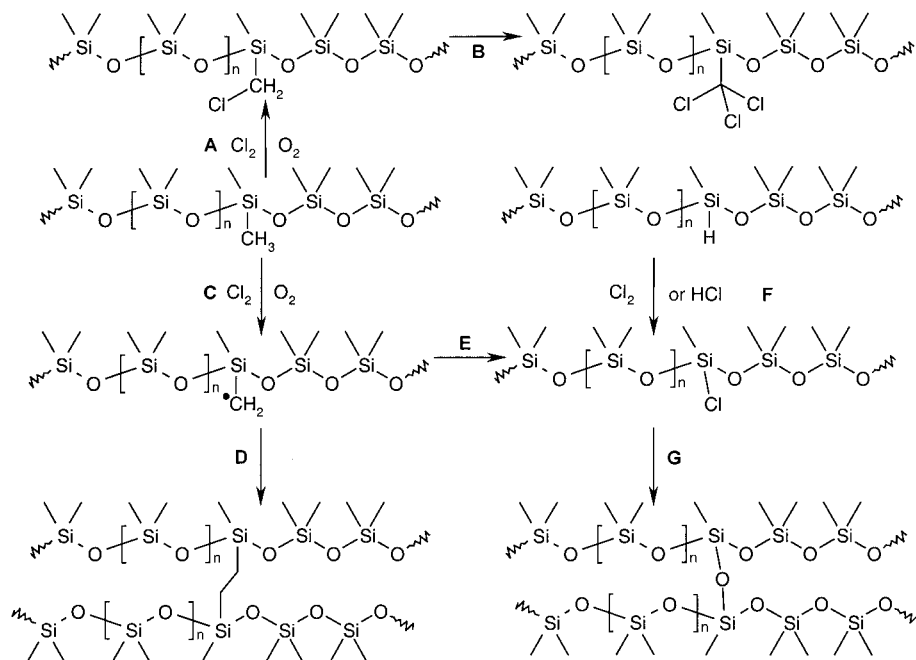


Figure 9 Crosslinking mechanisms.

acts very quickly with the HCl to give depolymerization as noted above.

FTIR analysis confirmed that PDMS was chlorinated after exposure due to the occurrence of the C–Cl bond in the spectra (Fig. 8). The FTIR spectra are also consistent with the formation of cyclic compounds and silicone crosslinking following exposure to Cl_2 . Due to the measurable range of the ZnSe crystal used in the analysis, the Si–Cl was, however, not detectable. This means that the bond may exist from chlorination, but this was not confirmed.

Chlorination and crosslinking of the silicone membrane are expected to have a profound effect on the behavior of the membrane. As the silicone becomes more rigid via both these mechanisms, the flux of the membrane should decrease. This is due to a denser polymer structure and reduction of the free volume. The solubility will also decrease when the polymer becomes denser.

Chain cleavage of the polymer chain, initiated by acid, should lead to higher fluxes and higher sorption coefficients, because of shorter polymer chains. These reactions can also be accompanied by loss of crosslinking, which results in increased swelling and weight loss due to evaporation of cyclic silicone by-products.

The permeation experiments showed that a highly crosslinked PDMS membrane can withstand Cl_2 exposure at elevated temperatures for

at least 60 days, even though the permeation rate became too low to be of industrial interest.

The general tendency is that permeation decreases over time for all gases examined once the PDMS membrane has been exposed to Cl_2 (Figs. 3–5). This observation is consistent with the increased chain rigidity and interactions due to side-chain chlorination and to increased density due to crosslinking. The decrease in permeation for the gas pair Cl_2 and O_2 in these membranes can easily be explained: Further crosslinking of the polymer chains gives a more dense structure, the polymer chains become more restricted to motion, and the free volume for transport will decrease within the polymer, resulting in a reduced permeability. The crosslinking can be catalyzed both by increased temperature and chlorine gas exposure.

With Cl_2 being a nonideal easily condensable gas, and O_2 the opposite, the decrease in permeability for both will follow different mechanisms depending on time and temperature, and may therefore result in even an increased selectivity, as a function of crosslink density, at certain intervals. The general tendency is, however, a slightly reduced selectivity over time for Cl_2/O_2 (documented in Fig. 5).

Figure 6 illustrates the temperature dependency of flux of Cl_2 in PDMS membrane material over almost 10 weeks. Referring to eq. (3), the permeabil-

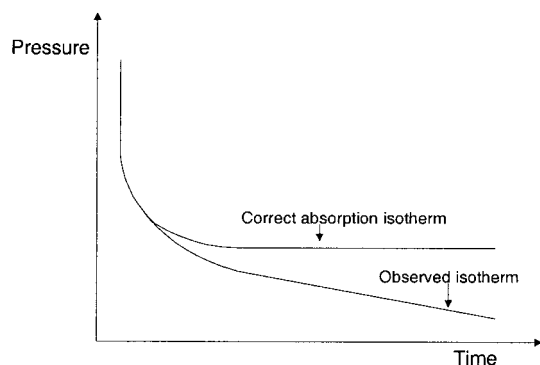


Figure 10 Typical absorption curve for Cl_2 sorption.

ity P is the product of the diffusivity coefficient D and the solubility coefficient S . If there were no changes in the material structure (like crosslinking or chlorination) there would still be a temperature effect on permeation [see eqs. (6) and (7)] with increasing permeabilities for O_2 , N_2 , H_2 , and decreasing permeability for Cl_2 ; this is well documented by Hägg¹ for experiments of short duration. The non-ideal nature of Cl_2 is confirmed by the negative value for ΔH_s found from the Arrhenius plot [Fig. 7a and eq. (6)]. The decreasing Cl_2 permeation with increasing temperature documented in the current work may thus be understood both as a function of the physical properties of Cl_2 and changes in the material, which depends on how long the material has been exposed to Cl_2 .

The permeation would be expected to increase if the membrane degraded via depolymerization leading to pin holes. This is observed after exposure of the membrane over 9 weeks at different temperatures (30–100°C). An alternative explanation for the increase in flux at long reaction times is an embrittlement of the membranes that leads to cracking, an additional source of pin holes. The effects of crosslinking and depolymerization can, in a perfect situation, cancel each other out until the film is either too thin or too rigid to be an efficient membrane.

The results from the sorption measurements are given in Table II. The sorption curve for Cl_2 in PDMS documented that additional chlorine will go into the membrane after sorption equilibrium has been reached; and that the chlorination reactions are taking place (illustrated in the schematic curve (Fig. 10)). The sorption measured at 80°C and 1 bar, was much higher than expected (Table II). The sorption performed under these conditions occurred over long time exposures, by which time degradation had be-

gun. At the higher pressure of 3 bar exposure, the time of absorption was shorter and the absorption equilibrium was reached more rapidly. Higher temperatures would speed up the reaction. The sorption increases with higher critical temperature of the molecules: $T_{\text{crit.Cl}_2} > T_{\text{crit.O}_2} > T_{\text{crit.N}_2} > T_{\text{crit.H}_2}$.¹

CONCLUSION

An understanding has been reached through documented experiments as to how the PDMS membranes change upon chlorine exposure: There is not a decomposition taking place if the membrane is fully protected, but rather a chlorination and probably additional crosslinking. The flux, however, decreases dramatically after a couple of weeks even at a mild temperature of 30°C. The reaction rate of the chlorination of PDMS increases with temperature. At the highest temperatures (above 80°C), the PDMS degraded with an attendant increase in flux and solubility coefficients. Chlorinated polymer chains have a high polarity giving strong interchain interactions, resulting in a denser polymer structure. The flexibility of rotation of the polymer chains are reduced and the glass transition temperature T_g will increase.

From the understanding reached by the documentation of the experiments, one must conclude that the PDMS is not very suitable as membrane material over longer time unless the temperature can be lowered significantly to slow down the chlorination reaction. Additionally, the membrane has to be totally protected from contact with humidity, particles, and steel since these factors catalyze degradation.

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