

# Transport Properties and Mechanical Behavior of Poly(Methyl-Phenylsiloxane) Membranes as a Function of Methyl to Phenyl Groups Ratio

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**ABSTRACT:** Membranes based on dimethyl and methyl-phenylsiloxane were synthesized and then fully characterized. Transport properties and mechanical behavior were determined as a function of different methyl/phenyl group ratios and the effects of these groups on results were established. Membrane transport properties were evaluated from *n*-hexane absorption studies. Static tensile stress–strain deformation measurements, stress–hysteresis determination, and stress–relaxation studies were performed to assess the mechanical behavior of these membranes. The results indicate that both physical–mechanical and transport properties are strongly affected by the methyl group content. The increase of the phenyl groups in the polymer chain impairs mechanical properties as a result of which decrease in crosslinking degree and gas permeability due to the diminution in free volume and penetrant solubility. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1624–1633, 2002

**Key words:** silicones; membranes; mechanical properties; structure–property relationships

## INTRODUCTION

Improvement of the already existing industrial gas separation technologies will be possible only through the synthesis of new polymer membranes that exhibit not only a high selectivity for specific gases and high intrinsic permeability, but also an adequate mechanical strength.<sup>1</sup>

There are many available types of materials from which membranes can be made, each with

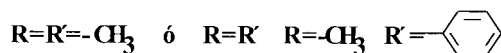
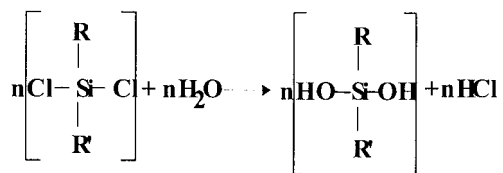
its own structural and chemical characteristics. However, if one considers the number of ways in which a permeating gas may interact with a given membrane, it is clear that finding a unified explanation for the complex transport processes occurring in gas permeation becomes a very difficult task.<sup>2</sup>

The variation in permeability of pure and mixture gases in glassy rubbery membranes was examined by several investigators.<sup>3–8</sup> However, the progress in the synthesis of new membranes is greatly slowed down at the present time by a lack of a sufficient understanding of the relationship between chemical structure of polymers and their gas permeability.<sup>9</sup> Furthermore, aiming to obtain high-performance industrial products, mechanical strength should also be controlled. Mechanical

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**Scheme 1** Hydrolysis of silanes with different functionalities.

properties of permeable membranes were practically ignored in the past, being rarely the main goal of studies concerning this kind of products,<sup>10</sup> although their determination is necessary because membranes in almost all commercial applications have to bear certain load levels.<sup>11,12</sup> However, membrane fragility and proneness to rupture make mechanical characterization a difficult problem.

Because of the characteristics of the permeation process, a membrane with good permeation properties implies high gas solubility and diffusivity. Under this requirement, the concept of supported solvent<sup>13</sup> appeared to be the most reasonable solution. On the basis of the preceding concept and the knowledge of the relationship existing between permeability and molecular and morphologic parameters of the membrane, it is concluded that polysiloxanes membranes are adequate model polymers. The polysiloxanes are the most important class of high-performance elastomers, and polydimethylsiloxane, with a repeat unit  $[-\text{Si}(\text{CH}_3)_2-]$ , is by far the most commonly used member of this class.<sup>11</sup> Silicone membranes have the appealing capability of being modified by chemical reaction (i.e., halogenation, dehydrogenation, substitution) to obtain products having physical properties (polarity, chain flexibility, spatial arrangement, cohesion forces) close by the chemical nature of the species present in the gas system.<sup>14,15</sup> By copolymerizing different siloxane monomers, it is possible to obtain polymers with a broad range of methyl/phenyl [Me/Ph] group ratios. The replacement of bulkier side-chain groups such as phenyl group in silicone membrane is concerned with gaining high selectivity.<sup>9</sup>

In this article, dimethyl and methyl-phenylsiloxane membranes with different [Me/Ph] ratios synthesized in our laboratory were studied. The resulting products were characterized by IR, picnometry, and thermal analysis. Transport properties, diffusion, and solubility were then evalu-

ated from *n*-hexane absorption studies. Mechanical behavior was also assessed by conducting static tensile stress-strain, stress-hysteresis, and stress-relaxation measurements.

Results showed that both transports and physical-mechanical behavior correlates with the [Me/Ph] ratio.

## EXPERIMENTAL

### Materials

Polysiloxane membranes for subsequent physicochemical and mechanical testing were prepared from the following materials. Silanes (98–99%) differing in functionality ( $RR'$ -Si-Cl<sub>2</sub>,  $R$ -Si-Cl<sub>3</sub>), tetraethylsilicate (98%), and dybutiltin dilaurate (95%) were supplied by Aldrich Chemical Co. (Milwaukee, WI), and ground kieselguhr was obtained from Fluka Chemika AG (Switzerland).

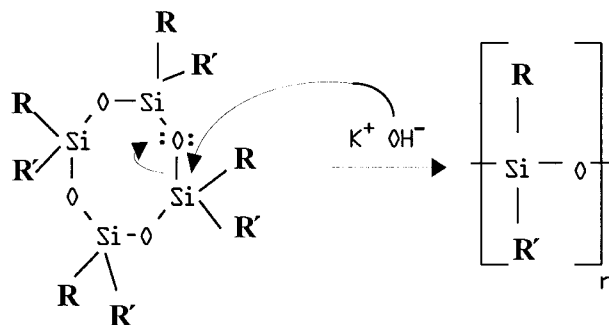
### Polysiloxane Synthesis

Polysiloxane membranes were prepared by the techniques reported by Braun et al.<sup>16</sup> and Grassie and MacFarlane<sup>17,18</sup> Briefly, the silanes were first hydrolyzed to the corresponding silanols, which are unstable and condense easily with elimination of water to form ( $-\text{Si}-\text{O}-\text{Si}-$ ) bonds (see Scheme 1).

Because of the tendency of the Si ( $RR'$ -O) unit to form cyclic structures, the hydrolysis of dichlorosilanes also yielded cyclic oligosiloxanes containing three to nine SiO units per ring, besides linear polysiloxanes.

Then, the cyclic siloxanes were converted to high molecular weight linear products by ring-opening polymerization with alkali (anionic polymerization; see Scheme 2).

To obtain mainly the suitable monomers for polymerization (trimeric and tetrameric dimeth-



**Scheme 2** Polymerization of the tetrameric cycle.

ylsiloxanes or methylphenylsiloxanes), the hydrolysis reaction was conducted under low temperature and concentration conditions. The latter conditions favor a higher efficiency in the production of cyclic compounds.<sup>17</sup> In the case of the dimethylsiloxane, temperature was kept below 20°C, whereas in the other cases, the temperature was kept close to 0°C. Temperature of the reactant mixture (i.e., distilled water, silanes, and ether) was monitored during the whole experiment.

The hydrolysis of dichlorodimethylsilane and dichloromethylphenylsilane with different [Me/Ph] ratios was performed in excess of water. These conditions increase the chances for the end chains to meet. Cycling of compounds with phenyl groups has shown steric limitations during reaction conditions. Therefore, if the proper length in the oligomeric molecules is met, then stable cycles with six to eight atoms develop.<sup>17,18</sup> The formation of the trimeric cycles (six atoms) and tetrameric cycles (eight atoms) is mainly due to the fact that no distortion of the hybridization angle ( $sp^3$ ) occurs. The hybridization angle  $sp^3$  is present in all the members (i.e., atoms) of the cycles. The amount of methyl groups, and the presence of linear and cyclic polysiloxane, was confirmed by IR spectroscopy as mentioned in previous work.<sup>13</sup>

### Film Preparation

The synthesized linear polysiloxanes (syrupy polymer) were crosslinked (curing process) at room temperature with tetraethylsilicate as crosslinking agent. Dibutyltin dilaurate was added as accelerator. Because on-service applications of silicone-based elastomeric membranes usually require solid filler to improve their poor mechanical properties, ground kieselguhr was incorporated as reinforcement. The solubility of the mixture (linear product) and the insolubility of the resulting silicone rubber (crosslinked product) in benzene were confirmed for all compositions. Soxhlet extraction experiences confirmed the absence of sol fractions. Films suitable for subsequent characterization (thickness between  $1.5 \times 10^{-2}$  and  $13.0 \times 10^{-2}$  cm) were obtained by extending the preparation over a flat glass platelet.

### Membrane Characterization

The [Me/Ph] ratio was determined by using Lady et al.'s<sup>19</sup> technique based on the intensity measuring of the methyl-silicon and phenyl-silicon

absorbance bands at 1260 and 1430  $\text{cm}^{-1}$ , respectively. The calibration curve used was reported elsewhere.<sup>13</sup>

Differential scanning calorimetry (DSC) was carried out on a Perkin–Elmer DSC 7. Two scans were performed by using a 10°C/min heating rate and a 320°C/min cooling rate (quenching) between runs. Thermograms were obtained in the range  $-140$  to  $40^\circ\text{C}$  under nitrogen purge. The glass transition temperature ( $T_g$ ) values were taken in the onset on the transition of second scans.

Membrane densities were determined by picnometry.

### Solubility and Diffusion Measurements

It is well known that sorption measurements allow the solubility and diffusion coefficient to be obtained.<sup>20</sup> The former is deduced from equilibrium values, whereas the latter is obtained from the unsteady state of sorption kinetics.

To estimate the absorption values, unsteady-state experiments were carried out in a Cahn-RG high vacuum electrobalance following a procedure described by Castro et al.<sup>21</sup> The samples were subjected to vacuum ( $1 \times 10^{-4}$  mmHg) in the thermobalance until their weight achieved a constant values. The arm region where the samples were placed was immersed into a thermostatic bath at a specified temperature and the temperature was registered. Once uniform temperature conditions were reached, a given amount of vapor was admitted in the system and the weight variation as a function of time was recorded. The temperature range investigated was from 0 to  $40^\circ\text{C}$ , whereas the applied pressure was up to 600 mmHg using *n*-hexane vapor.

The absorption values were then used to determine the solubility and the diffusion coefficients, as follows:

The solubility of the vapor into the polymer was determined when the weight record remained unchanged. This procedure was repeated until the maximum-allowed value of pressure was reached, ensuring that the vapor condensation took place.

The diffusion of gas through a membrane can be described by Fick's first law, which takes the following form for one-dimensional transport in a normal direction to the membrane area:

$$q = -Dx\partial C/\partial X \quad (1)$$

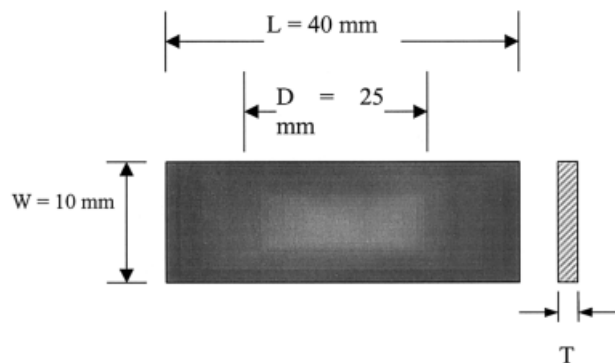


Figure 1 Geometry of the test samples.

where  $q$  is the flux of gas, which goes through the membrane per unit of area,  $D$  is the diffusion coefficient for a specific gas-membrane system at a given temperature, and  $C$  is the concentration of gas at position  $X$ . The diffusion coefficients,  $D$ , were computed by using the free boundary model proposed by Destéfani et al.<sup>22</sup> as a function of the absorbing species from the weight variation data as a function of time.

The permeation of gases through polymer membranes at temperatures above their glass transition, as in the present study, generally occurs by a solution-diffusion mechanism. This mechanism implies that the permeation process is controlled by the molecular diffusion of the penetrant gas in the membrane matrix, while, at the same time, the penetrant dissolved at the membrane interfaces is in solution equilibrium with its adjoining gas phase.

It can be shown that  $P$  is the product of a mean diffusion coefficient  $D$  (a kinetic factor) and of a solubility  $S$  (a thermodynamic factor)<sup>20,23</sup>:

$$P = S \times D \quad (2)$$

For simplicity, to compare the influence of methyl content on transport properties, only results obtained at 30°C are shown throughout the article.

### Mechanical Characterization

Mechanical properties measurements included stress-strain, stress-relaxation, and tensile hysteresis. All mechanical testing was conducted in a 4467 Instron universal machine at room temperature. The geometry of the test samples is shown in Figure 1. Clamps especially designed for this kind of rubber (mechanically weak) were used.

Stress-strain measurements were carried out under displacement control in axial direction. En-

gineering strain,  $\epsilon$ , was calculated using eq. (3) under the assumption of a homogeneous deformation. The displacement variation,  $\Delta L$ , was determined directly from the crosshead displacement rate (50 mm/min) because the use of the mechanical extensometer was practically impossible:

$$\epsilon = \Delta L/L_0 \quad (3)$$

The stress was computed as the axial force divided by the initial cross-sectional area,  $A_0$ . Some experiments were conducted up to the rupture point of the sample and characteristic nominal stress-strain traces were determined for each individual composition. Young's modulus,  $E$ , was calculated from the straight-line portion of the  $\sigma$  versus  $\epsilon$  curves (at  $\epsilon \rightarrow 0$ ) using eq. (4),

$$E = \sigma/\epsilon \quad (4)$$

and rupture stress and elongation at break determined from the final point of the curves. The area under the stress-strain curve corresponds to the energy or rupture,  $E_r$ , which is a standard measure of elastomer toughness.<sup>24</sup>

Another important aspect related to internal structure is the relaxation stress, which represents the change of the stress as a function of time at a constant deformation and temperature. Stress-relaxation measurements were performed by imposing 25, 50, and 75% initial elongation levels on samples at a crosshead speed of 500 mm/min and then letting them relax. Nominal stress and time was continuously monitored to obtain stress-relaxation data. The ultimate values were read after 10 min. The curves were fitted to the following empirical relation as suggested in literature<sup>5</sup>:

$$\frac{\sigma(t)}{\epsilon_0} = E_{rL}(t) = Kt^{-n} \quad (5)$$

where  $K$  and  $n$  are constant,  $E_{rL}$  is the relaxation modulus,  $\epsilon_0$  is the initial deformation,  $\sigma$  is the stress (MPa), and  $t$  is the time (min).

The exponent  $n$  in eq. (5) is a nondimensional number that can be viewed as a measure of the relative importance of the elastic and viscous contribution to relaxation.<sup>5</sup>

Hysteresis cycles caused by repeated loading and unloading at different elongation levels (25–100%) were also performed. To ensure that results are strictly comparable, each test was driven with a new specimen that was submitted

**Table I Physical Properties as a Function of Chemical Composition**

%CH <sub>3</sub> -%Ph	$\rho$ [g/cm <sup>3</sup> ]	$T_g$ [°C]
100-0	0.960	-125
85-15	1.073	-95.2
70-30	1.187	-65
50-50	1.342	-26.7
30-70	1.448	—

to increasing amounts of strain and allowed to relax at zero load for 3 min before starting each loop. The hysteresis percentage for a given cycle was calculated from the ratio of the area bounded by the loading-unloading to the total area under the loading curve.<sup>25</sup>

## RESULTS

### Characterization

The physical characteristics of the prepared poly-methylsiloxane membranes as a function of chemical composition are shown in Table I.

It can be observed that the density decreases with the methyl content and that the 100% methyl groups value is very close to the one reported by Stern et al. (0.971 g/cm<sup>3</sup>) for similar polymers.<sup>1</sup>

Consistent with previous statements,<sup>9</sup>  $T_g$  values increase with the incorporation of bulkiness side-chain groups (phenyl group content).

### Mechanical Behavior

Uniaxial stress-strain traces as a function of methyl group percentage are shown in Figure 2.

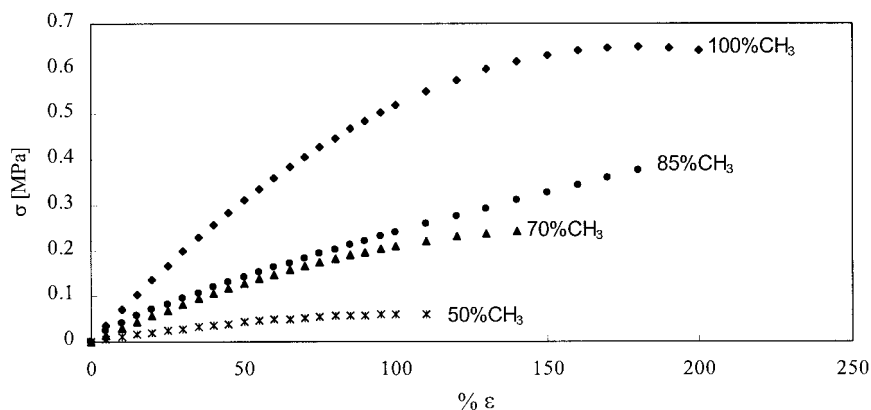
**Table II Mechanical Properties as a Function of Chemical Composition**

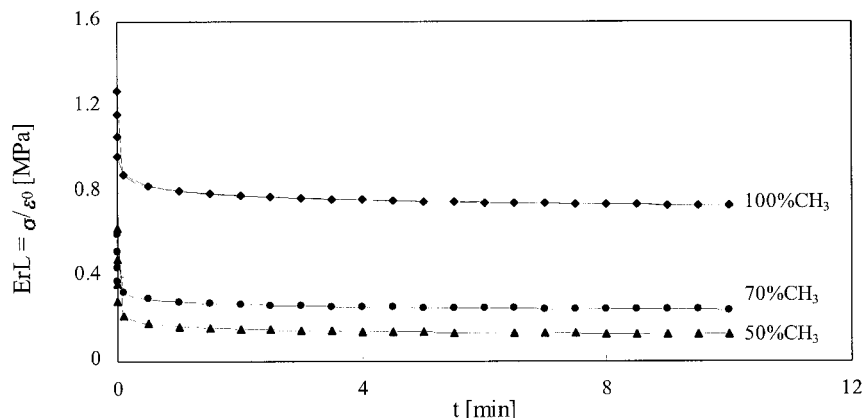
%CH <sub>3</sub> -%Ph	$E$ [MPa]	$\sigma_B$ [MPa]	$\epsilon_B$	$E_r$ [J/mm <sup>3</sup> ]
100-0	1.44	0.640	2	120.77
85-15	0.30	0.375	1.8	68.33
70-30	0.25	0.244	1.4	29.85
50-50	0.08	0.060	1.1	4.73

Young's modulus, which represents mechanical response at low deformation levels, ultimate properties (stress and elongation at break), which represents mechanical response at high deformation levels, and energy of rupture which is a measurement of rubber toughness are shown in Table II. The values of Young's modulus<sup>5</sup> and ultimate properties<sup>11</sup> for 100% methyl are within the values published in literature. From the analysis of these results, it clearly emerges that these membranes are mechanically weak and that the presence of phenyl groups deteriorate even more mechanical properties.

Relaxation results are shown in Figure 3 and Table III. Normalized stress [ $\sigma(t)/\epsilon_0$ ] decay always takes place up to a certain percentage of the original value (limiting value). The limiting stress value was directly proportional to the applied initial deformation and to the number of methyl groups (degree of crosslinking) for all membrane compositions assayed. Consistently, exponent  $n$  of the kinetic expression decreases as the percentage of methyl groups increases (Table III).

Hysteresis experiments [Fig. 4(a,b), Table III] show the effect of stress-strain cycling on these membranes. These curves exhibit stress-softening phenomenon<sup>26</sup> and irreversibility. Significant hysteresis loops (quantified as hysteresis percent-

**Figure 2** Stress-strain curves.



**Figure 3** Normalized stress  $E_{rL}$  versus time at different methyl group contents.

age) as well high permanent set (quantified as the percentage of residual deformation) is observed. Both magnitudes increase with the level of the deformation applied and phenyl groups content.

### Transport Properties

The results obtained from transport experiments at varying temperatures and [Me/Ph] ratios are described in Figures 5-9.

Figure 5 shows the absorption isotherms for a membrane with 100% methyl content performed at different temperatures. This result clearly demonstrates that solubility follows the usual increasing trend with the decrease in temperature.<sup>20,27</sup> Although not shown here, the same experiments conducted on the other composition led to the same conclusion.

Figure 6 presents the results regarding solubility variation with pressure for different [Me/Ph] ratios at 30°C. It appears that the change in the chemical nature of the membrane precursor polymer alters solubility: the higher the content of methyl groups, the higher the solubility.

Figures 7 and 8 show the variation of solubility and diffusion values at 30°C and 60 mmHg with the change of membrane chemical composition.

**Table III** Viscoelastic Properties as a Function of Chemical Composition

%CH <sub>3</sub> -%Ph	$n$	Hysteresis (%)
100-0	0.0402	43.98
85-15	0.0524	57.54
70-30	0.0661	61.49
50-50	0.1929	88.90

These coefficients display an increasing trend with the increasing methyl group content.

The variation of the permeation coefficient as a function of the membrane composition is shown in Figure 9. It is seen that the value of the permeability coefficient decreases with the decreasing methyl group content.

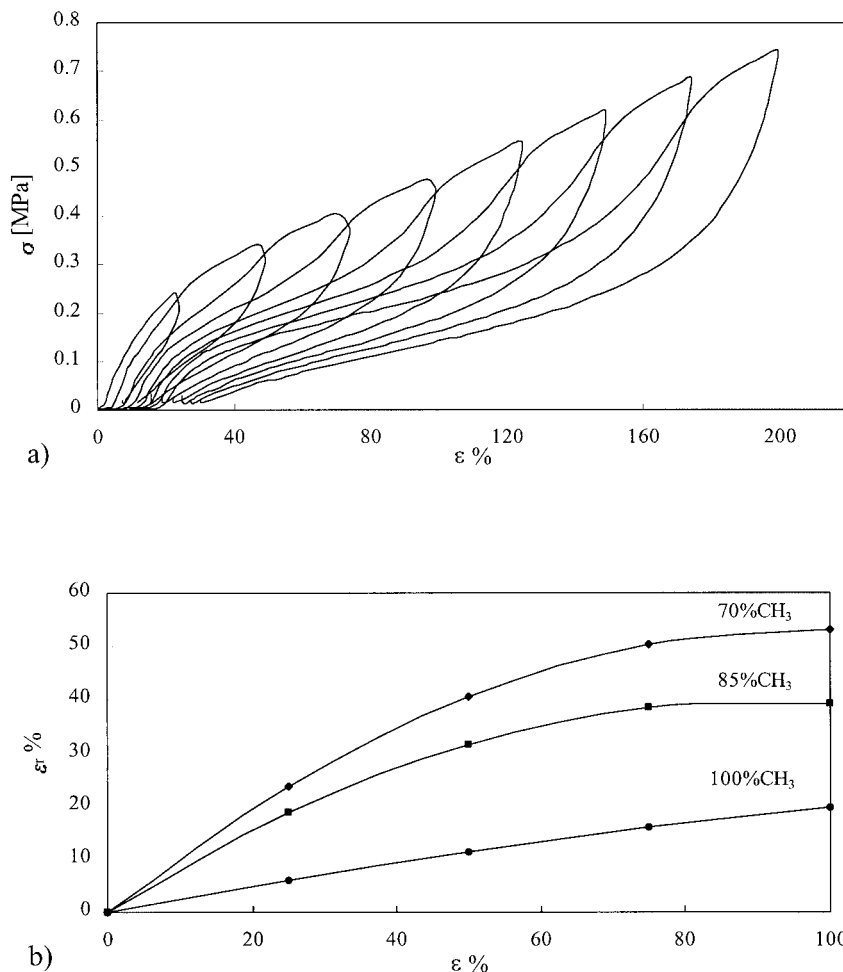
### DISCUSSION

The differences in the chemical composition of the synthesized polymers are reflected in the notable differences found in the physical-mechanical behavior and transport properties.

The substitution of methyl groups by bulkier functional groups in the side chain (such as phenyl group) led to products with relatively high  $T_g$  and density but low Young's modulus (Table II). The free volume was not affected by the decrease of the crosslinking density, and the phenyl groups did not produce significant network distortion. Intermolecular distances between methylsiloxane chains are greater than between hydrocarbons because intermolecular forces are smaller,<sup>28</sup> inducing a marked decrease in the polymer-free volume.

The presence of the methyl groups in the polymer chain leads to higher crosslinked networks because of the type of the carbon atom hybridization associated with these groups. As predicted by the rubber elasticity theory (eq. 13.40 in ref. <sup>5</sup>), the degree of crosslinking controls the rubber's stiffness (Young's modulus), irrespective of the reduction of free volume associated with the concentration of bulky substitutes.

According to Stern statements,<sup>1,9</sup> chain flexibility is at loss with phenyl groups substitution, as demon-

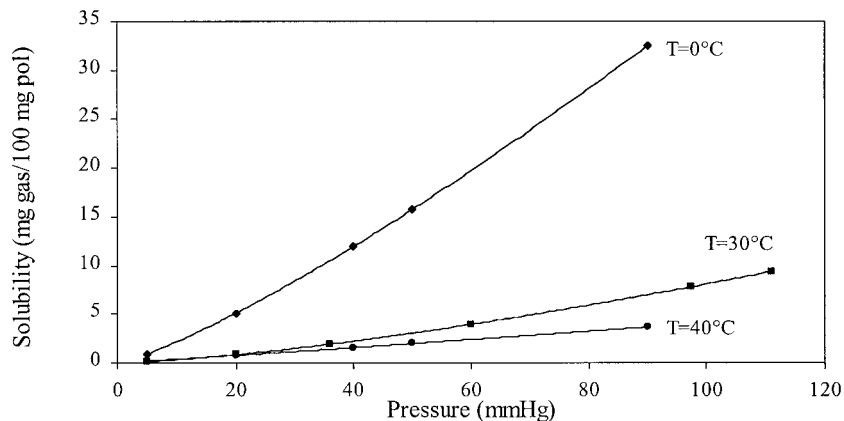


**Figure 4** (a) Stress–hysteresis cycles of polysiloxane with 100% CH<sub>3</sub> versus elongation and (b) residual strain as a function of elongation at different methyl group contents.

strated with the increasing trend in  $T_g$  values (Table I), which are in direct relation to chain stiffness. Van Krevelen (eq. 18.12a in ref. <sup>5</sup>) shows that elastomers (rubbery polymers) with  $T_g < 298$  K follow eq. (6):

$$p = 7.5 - 2.5 \times 10^{-4}(298 - T_g)^2 \quad (6)$$

where  $p$  is a characteristic parameter for the polymer, which is as an index of the molecular stiff-



**Figure 5** Absorption isotherms for a membrane with 100% methyl content at different temperatures.

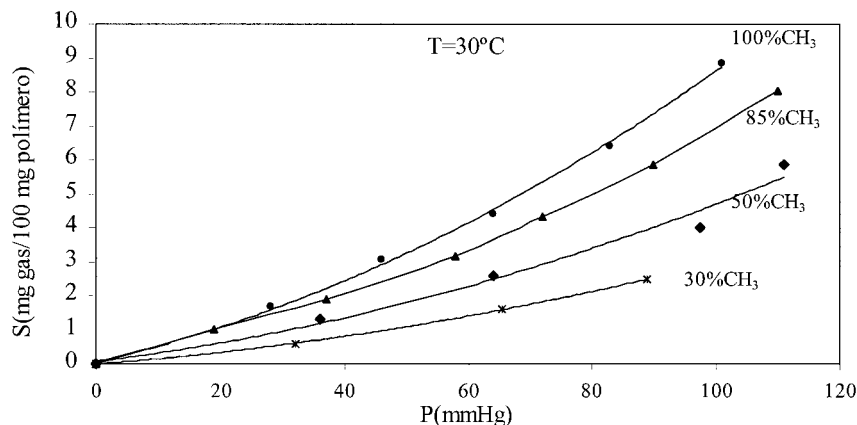


Figure 6 Solubility variation with different methyl group contents.

ness of the polymer,  $(298 - T_g)$  is the thermal distance between  $T_g$  and room temperature for rubbers. These thermal distances are connected with the fractional free volume (f.f.v.) of the polymer. Hence, a decrease in  $T_g$  implies an increase in f.f.v. It appeared clear that in our polymers  $T_g$  is controlled by the phenyl group (bulkiness groups) content, which in consequence also determined the polymer-free volume.

The analysis of stress-strain curves (Fig. 2 and Table II) revealed very low values of ultimate properties,  $\sigma_B$ ,  $\epsilon_B$ , and  $E_r$ , indicating that these membranes are mechanically weak. Elongation is the effect brought about by uncoiling the chains through axial stretching; when the chains have exceeded the maximum stretched length, breakage will occur. The overall best mechanical properties (see ultimate properties) that depend on the internal material cohesion forces were dis-

played by the most crosslinked samples (high methyl group's content). This constitutes clear evidence that the contribution to mechanical strength of bulkier groups in the side chains results is negligible, consistent with the idea that the influence of the glass transition temperature (higher at high phenyl groups content) becomes less pronounced as crosslinking progresses.

Relaxation phenomena seem to be intrinsically related to the chemical structure. Relaxation behavior can be explained by a domination of the elastic forces over the viscous forces. In the materials tested, the elastic forces are originated by crosslinking between chains (covalent bonds) and the viscous forces are related to the weak interactions (type Van der Waals) as described by the  $n$  parameter (see eq. (5) and Fig. 3). Small  $n$  values imply large relaxation modulus,  $E_{rL}$ , and are in direct relation with the degree of crosslinking.

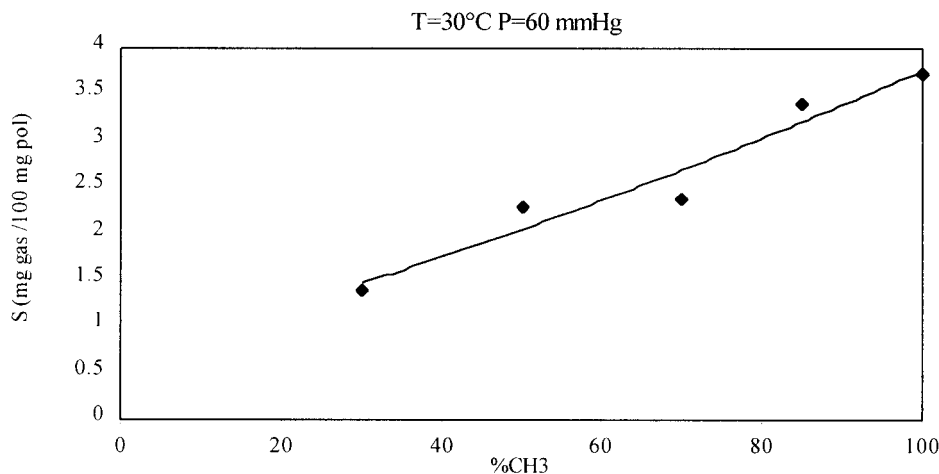
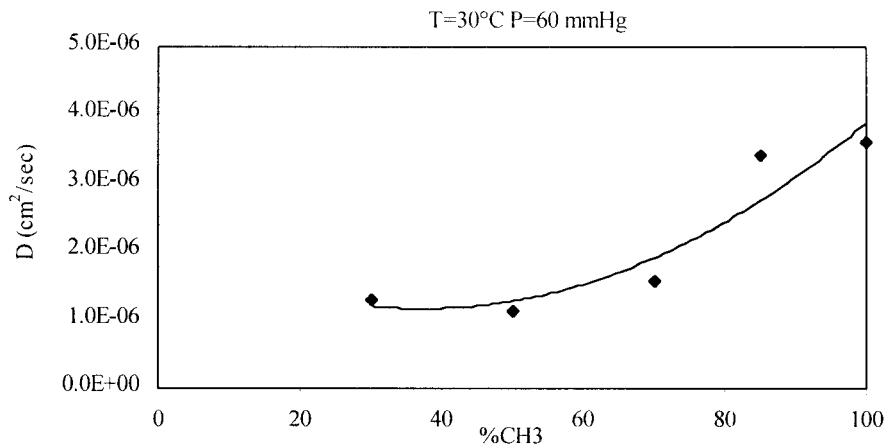


Figure 7 Solubility versus methyl group content at 30°C and 60 mmHg.





**Figure 8** Diffusion versus methyl group content at 30°C and 60 mmHg.

The always-existing limiting value confirmed that even products with low concentration of methyl groups are tridimensional networks.

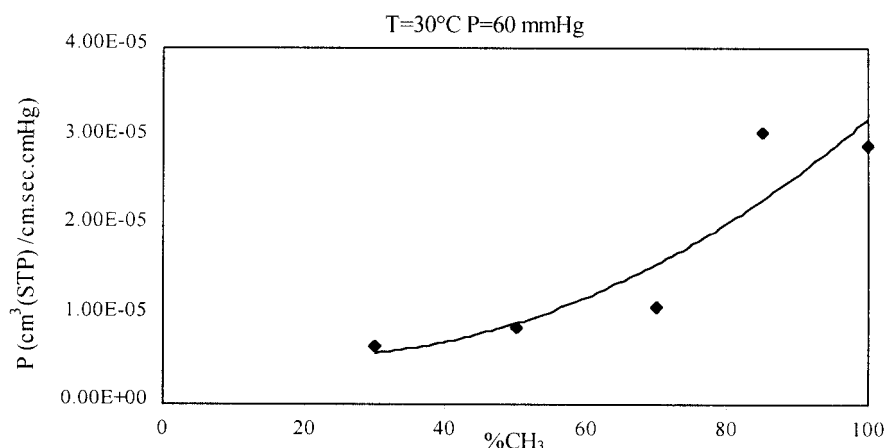
The importance of the hysteresis phenomena found may not be attributed simply to typical viscoelastic behavior (internal friction of molecules during the stretching process) and detachment of the filler particles as usually reported in rubbers.<sup>26</sup> The loss of the energy in the hysteresis cycle at the different elongations is due to the weakness of the network chain, judged from the very low ultimate properties (Table II), and rupture during deformation cycles is plausible. At a relatively large degree of applied deformation, disruption of covalent bonds occur, preventing the material to recover the original state. Obviously, energy losses are larger in material with high phenyl content because the number of intermolecular covalent linkage which represent the mainly contribution to material cohesion are highly reduced.

The permeant capacity related to the particular species is determined by concomitant solubility and diffusion system performance.

The changes in the transport properties are highly affected by the chemical nature of the permeant and membrane, as well as by change in the built network. The differences in the network structure were revealed by the physical mechanical analysis. For instance, the loss of flexibility in the polymeric chains as well as the occupation of available free volume is reflected in the poor diffusivity and solubility displayed by the membrane with a high percentage of the phenyl groups.

The enhanced solubility coefficient displayed by polysiloxane membranes synthesized at a high methyl group percentage may be also associated with a large chemical affinity between penetrant and membrane.

The cost of obtaining membranes with high selectivity<sup>9</sup> (i.e., products with high bulky substi-



**Figure 9** Permeability versus methyl group content at 30°C and 60 mmHg.

tuting contents) is not the only well-known loss in permeability but also a large detriment of mechanical behavior. Values of the ultimate properties (ultimate strength, maximum extensibility, and energy of rupture), as well as the performance of the membranes submitted to a cycling loads, are being seriously compromised with the diminution of crosslink density. This harmful effect can seriously limit service life.

## CONCLUSION

From the results presented here, the following conclusions can be drawn:

It was possible to synthesize polysiloxanes at varying [Me/Ph] ratio contents and crosslinking degrees by starting from silanes of different functionality. Free volume and internal cohesion of the products did not vary concurrently.

The obtained membranes showed important differences in the transport and mechanical properties associated with the differences in the network structure and chemical nature. The overall best mechanical and transport properties were displayed by samples with high methyl groups content.

The crosslinking density (in direct relationship with the methyl group content) controls mechanical properties.

The relative amount of phenyl groups are responsible for fractional available free volume,  $T_g$ , membrane density, and diffusion rate.

High penetrant solubility is linked to large chemical affinity with methyl group content and available free volume.

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