Prospects of Siloxane Membrane Technology for Gas Separation — A Review

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Siloxane membranes have been long utilized industrially for the separation of gas mixtures due to its very high permeation rate. But the selectivity of this membrane for a particular gas mixture is very low. In order to improve its selectivity value without drastically reducing its permeation rate, lot of literature based on the chemical structure modifications is available. These modifications often lead to an improvement of selectivity value at the cost of permeability value or vice-versa. This review deals with the factors affecting the permeability value and an up-to-date chemical modification of siloxane membranes and its transport parameters.

Keywords: Siloxane membrane, Gas separation, Transport parameters

Introduction

The discovery of vulcanization by Goodyear in 1839 transformed natural rubber into an essential commodity. Worldwide rubber commodities, such as balloons, bicycle tires, auto tires, etc., led to the puzzling observation of air loss from inflated rubber containers in the absence of any detectable wall defects. Graham had reported that rubber is permeable to different gases in different degrees and is independent of gas viscosity. Many additional aspect of research on gas and vapour permeation through rubbers, whose principal objectives were to understand the cause of gas leakage and find means to eliminate it, were conducted between 1877-1945. The research work carried out during this period established that rubber was both gas / vapour permeable and selective, and it also laid the ground work for our understanding of the mechanisms and kinetics of molecular transport through polymers. The past decade has seen the rapid development of important laboratory and industrial applications of permselective synthetic polymeric membranes for molecular separations. Cryogenic distillation, adsorption, and chemical separation are well established technologies in this field. More recently, membranes have joined the list of available technologies for the separation of gases. Membrane separation offers the specific advantage of low energy use, simplicity, ease of operation, limited space requirements as well as economic benefits. Although membrane separation is not expected to completely replace the established technologies, it offers significant benefits and will be a competitive system in specific existing applications as well as in new applications.

The chemical structures of these polymeric membranes range from simple hydrocarbons (like polyethylene or polypropylene) to polar structure (like polyamides) or ionic structures in which cations (or) anions are attached to the backbone. Performance of these membranes depends upon the physicochemical interactions (ionic interactions, dipolar interactions and Vander Waal forces) between the permeation species and the membrane materials. The potential application of a polymeric membrane for gas separation depends on two parameters, viz., permeability, the ability of gaseous molecule to pass through the membrane, and selectivity, the ability of the membrane to selectively allow a particular gas molecule to pass through it from a mixture of gases. For commercial application, these two parameters should be as large as possible, however, majority of the polymeric membranes show a typical trade off behaviour i.e., high permeability value combined with low selectivity value and vice versa. Figure 1 shows a typical tradeoff behaviour of different membranes for oxygen/nitrogen gas mixture. Separation of gaseous and volatile liquid mixture by membrane permeation continues to be the subject of

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intensive research. Some of the polymeric membranes that have been widely used for gas separation are shown in Table 1.

**Transport Mechanism**

Gas separation using polymeric membranes function as a simple method for purifying commercially important and often difficult to separate gaseous mixtures. In their ideal form, membrane appears to act as a molecular scale filter that produces permeate containing pure A and a non-permeate containing pure B from a gaseous mixture of A and B. Real membrane can approach this simplicity and separation efficiency by involving more complex operations of recycling some of the permeate (or) non-permeate stream for high purity requirements, since perfect separation of A and B typically cannot be achieved in a single pass\(^5\).

![Transport Mechanism Diagram](image)

**Table 1 — Some of the polymeric membranes used for gas separation**

<table>
<thead>
<tr>
<th>Structure</th>
<th>( PO_2 )</th>
<th>( PN_2 )</th>
<th>( PCO_2 )</th>
<th>( PCH_4 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cellulose acetate" /></td>
<td>0.82</td>
<td>0.15</td>
<td>4.75</td>
<td>0.15</td>
<td>11</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>19.4</td>
<td>5.8</td>
<td>116</td>
<td>12.4</td>
<td>12</td>
</tr>
<tr>
<td>Polysiloxane</td>
<td>800</td>
<td>400</td>
<td>3800</td>
<td>1200</td>
<td>13</td>
</tr>
<tr>
<td>Polymethyl silylepropyne</td>
<td>9710</td>
<td>6890</td>
<td>37,000</td>
<td>18,400</td>
<td>14</td>
</tr>
</tbody>
</table>
Gas separation, in general, can be performed using membranes based on any one of the three general transport mechanisms, viz. Knudsen diffusion, Molecular sieving, and Solution-diffusion mechanisms (Figure 2). Knudsen diffusion relies on separation based on the difference in the molecular weight of the diffusing gases. In this separation the selectivity for a particular gas is proportional to the square root of the inverse ratio of the molecular weight of permeating gas mixture. Molecular sieving mechanism depends on the pore diameters that are created in the membranes, which are inbetween the size of the gas particle to be separated. Gas molecule with smaller size pass readily compared to the larger size molecules. In solution-diffusion mechanism, there is no continuous passage of gas molecule through the membrane but it largely depends on the penetrant-scale transient gaps formed in the polymer matrix due to thermally agitated chain segmental motion. The penetrants undergo random jumps due to higher concentration at the upstream face than the downstream face, a diffusion flux occurs towards the downstream face.

The majority of the membranes that are studied in the laboratory and the membranes that are currently commercially available operate according to the solution-diffusion mechanism. The model concept for solution-diffusion mechanism was first articulated by Graham qualitatively. According to his concept the material transport occurs in three steps, viz. sorption, diffusion, and desorption. The rate of gas permeating through the membrane depends on these three parameters. Consistent with Graham's view of the process the thermally agitated motion of chain segment comprising the polymer membrane generates penetrant-scale transient gaps by which sorbed penetrants diffuse from up steam to the down stream face of the membrane.

A quantitative relationship for the diffusion of gas through a non-porous membrane was given by Fick. He observed that the quantity of gas (J) which passes through the membrane per unit time and unit area is proportional to the difference in pressure between the input side (P1) and permeate side (P2) and is inversely proportional to the thickness of the membrane (d).

\[ J = \frac{(P_1 - P_2)}{d} \]

\[ J = P_e \frac{(P_1 - P_2)}{d} \]

The proportionality constant, called permeability coefficient of the given polymer membrane for the given gas X, it is a substance.

![Figure 2](image-url)
specific quantity and is characteristic for each membrane material, \( V \) – permeate volume of the gas, 
\( d \) – membrane thickness, \( A \) – membrane area, \( t \) – time, and \( \Delta P \) – pressure difference between input and permeate sides. Generally the permeability coefficient was expressed in Barrer and the unit is \([cm^2(STP)cm/cm^2s cm Hg] \times 10^{10}\).

Von Wroblewski\(^{22}\) showed that the permeability coefficient (\( P \)) can be viewed as the product of solubility coefficient (\( S \)), a thermodynamic parameter, and diffusion coefficient (\( D \)), a kinetic parameter.

\[ P = D \times S. \]

Experimental methods and apparatus for the measurement of \( P, D \) and \( S \) have been described by many investigators\(^{25-26}\). Critical discussion, including description and analysis of many techniques with methods of calculation and sources and minimization of errors has been given by Felder and Huvard\(^{26}\).

The selectivity \( \alpha \) (also called separation factor) of a membrane material for a pair of gases \( X \) and \( Y \) is defined as the ratio of the permeability coefficients for \( X \) and \( Y \):\(^{27}\)

\[ \alpha = \frac{P_X}{P_Y}. \]

**Theoretical Approach**

The theoretical approaches for the description of gas permeation/diffusion through the polymeric membranes have been discussed in numerous reviews\(^{28-31}\). The permeation of a gas molecule through a polymeric membrane largely depends on the nature of the gas molecule and its interaction with the polymer in question. The molecular structure related factor, such as polarity, hydrogen bonding, cohesive energy, density, chain flexibility, steric hindrance, side group substitution, and crystallinity all affect the permeation process in some manner\(^{32-35}\). Unfortunately, these factors because of their interrelating nature are not easily separable from one another. Thus, it is difficult to isolate the individual effects.

Pye and Hoehn\(^{36}\) at Dupont derived a qualitative rule based on their pioneering work. According to them, “when changing the structure within a family of polymers inhibiting intersegmental packing, while simultaneously hindering the backbone mobility, tend to produce a desirable trade off between productivity and permeability changes”. Currently, this is the most reliable guide for understanding the structure-permeability studies of a given family of polymers.

Increased packing inhibition can be detected by an increase in the free volume fraction in the polymer matrix\(^{37-38}\). Inhibition of segmental and sub-segmental motion can be detected spectroscopically by the increase in glass transition temperature (\( T_g \)) or sub-\( T_g \) (\( T_r \)) values\(^{37-39}\).

The macroscopic space which a polymer occupies was not completely filled by its chains and gaps were formed which cannot be filled due to conformational constraints. A fraction of these gaps are large enough to accommodate gas particles and the sum of these gaps are called the specific free volume\((V-V_o)\)\(^{40-41}\). The specific free volume can be obtained from the difference between the total specific volume \((V)\) and the occupied volume \((V_o)\). The total specific volume can be obtained from the experimentally determined densities of the membrane and the occupied volume, primarily comprises the electron cloud of the atoms of the polymer, can be estimated from group contribution method\(^{42}\). The ratio of the specific free volume to the specific volume of a polymer sample is defined as the fractional free volume \((FFV)\). This free space is mobile and exists as more or less random disconnected packets\(^{43-44}\).

\[ FFV = \frac{(V - V_o)}{V}. \]

It was shown that the permeability and diffusion coefficients do not correlate with the density or the glass transition temperature of the membrane. There is, however, a relatively good correlation between the inverse of the fractional free volume in the polymer and the logarithm of the permeability coefficient\(^{45-46}\). As the free volume of amorphous polymer is generally much larger than that of crystalline polymers, mostly amorphous polymers were used for gas separation.

Theoretical model, such as that of Pace and Datynor\(^{47}\) which takes the structure of polymer chains into account are more suitable. According to them the transport of gas particles occur by leaps between the gaps present in the polymer matrix. The thermal motion of certain segments of the polymer chain open up a sufficiently large channel to a neighboring gap. The gas particles can then diffuse through these channels. Once the channel closes afterwards the jump has been successfully concluded. In this scenario the selectivity of a membrane material depends on the control of these leap channels. Large openings due to substantial segment motions permit unrestricted passage to all gas particles, whereas more
limited motion permits the passage of smaller species move frequently than of large particles. Therefore, by modifying the local chain flexibility by introducing substituents or by varying the length of the critical segments within the repeat unit of the polymer allows the optimization of the polymer for a given separation task.

The facts presented so far conclude that significant improvements in permeability and selectivity of a polymer can no longer be achieved by more or less random structural variations of basic structures. A plausible suggestion for further development of polymer membrane stems from Koros et al.\textsuperscript{54}. They recommend control of the mean diameter and the distribution of diameter of the gaps between the polymer chains, which make up the free volume. According to the suggestion from Koros et al., a narrower distribution of gap diameter could be achieved with a certain type of polymer architecture. Polymer chain that consists of alternating bulky and flat units should be preferentially packed in such a manner that the bulky groups act as spacers and prevent tight packing of the flat groups and thus leave gaps in the vicinity of the flat chain segments. The effect of the various molecular structural factors on the diffusion constant can be examined in terms of a simplified free volume concept.\textsuperscript{42} For instance the addition of a side group to the backbone of a polymer chain could cause a change in its chain stiffness. At the same time, it may have altered the polarity and hydrogen bonding characteristics of the chain. As a result of the changing molecular interactions and chain to chain distance, it may bring about variation in free volume. Hence the gas diffusivity of the modified polymer chain would take on a different value at the new free volume.

Although considerable data and general correlations relating structure and permeability exists, there are no truly quantitative relationships to guide detailed structure-permeability optimization. The review studies how introduction of different functional groups affect the permeability and selectivity value for poly(dimethylsiloxane) membrane.

**Poly(dimethylsiloxane) (PDMS) Membrane for Gas Separation**

The application of siloxane polymers in the area of synthetic membrane is of special interest because of very high permeation rates exhibited by PDMS for a range of gases.\textsuperscript{37} The limitation with this polymer is its poor selectivity value for a particular gas in a mixture of gases. It is more permeable to many organic vapours than to supercritical gases, such as nitrogen in membrane-based vapour separation application.\textsuperscript{39} It has unique properties, such as thermal stability, hydrophobicity, and the flexibility for the incorporation of different functional groups into Si-O linkage.\textsuperscript{3,51,52} For commercial application, a membrane should have a permeability value of at least one Barrer and a selectivity value of five.

Merkel et al.\textsuperscript{13} studied the permeability of poly(dimethyldisiloxane) (PDMS), filler free composite membrane crosslinked at 30°C. The values obtained by them for different gases are shown in Table 2. It is seen from Table 2 that the solubility coefficient affects the permeability value much more than the diffusion coefficient. Generally, diffusion selectivity increases as the difference in the relative size of two penetrants increases and the solubility selectivity increases as the difference in condensability between the two penetrants in a mixture increases.\textsuperscript{56} Hence, trade off exists between solubility selectivity and diffusivity selectivity with the overall selectivity depending on the relative magnitudes of these two terms.

Based on the size (Table 3) of the permeating gas the permeability coefficient for the smaller size permanent gases, like H\textsubscript{2}, O\textsubscript{2} and N\textsubscript{2} were expected to have high value compare to the larger size more condensable gases, like CO\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, and C\textsubscript{4}H\textsubscript{10}. But condensable gases were observed to have very high permeability value in PDMS. When penetrant pressure and therefore penetrant concentration in the polymer increases the tendency to plasticize a polymer matrix increases, particularly for a strong sorbing penetrants. Plasticization refers to an increase in penetrant diffusivity resulting from increased local

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>Permeability [Barrer]</th>
<th>Solubility [cm(^3)(STP)/cm(^2).atm]</th>
<th>Diffusivity [cm(^2)/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>890 ± 30</td>
<td>0.05 ± 0.008</td>
<td>140 ± 5</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>800 ± 20</td>
<td>0.18 ± 0.01</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>400 ± 10</td>
<td>0.09 ± 0.008</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>3800 ± 70</td>
<td>1.29 ± 0.01</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>1200 ± 40</td>
<td>0.42 ± 0.01</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}</td>
<td>3300 ± 100</td>
<td>2.2 ± 0.02</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{10}</td>
<td>4100 ± 300</td>
<td>5.0 ± 0.07</td>
<td>5.1 ± 0.3</td>
</tr>
</tbody>
</table>
can slightly compress the polymer matrix, thereby reducing the amount of free volume available and reducing penetrant diffusion coefficients. As a result of interactions between these factors the permeability coefficient of low sorbing penetrants, such as H₂, which do not plasticize PDMS have low permeability value compared to the more soluble penetrants which induce significant plasticization.

From the results, one can observe that a rubbery polymer, such as PDMS has poor ability to sieve molecules based on size, making diffusivity a weak function of penetrant size. Consequently, for rubbery polymer the overall selectivity is often governed by difference in penetrant solubility. Critical temperature is used as a scaling factor for penetrant condensability, hence penetrants with higher critical temperature are more soluble in polymers. Many researchers have attempted to improve the selectivity value for oxygen/nitrogen gas mixture without drastically reducing the permeation coefficient by functionalization of PDMS with different groups.

**Functionalized Poly(Organosiloxane) Membrane for Gas Separation**

Stern et al. have studied the permeability value for different hydrocarbon functionalized poly(dimethylsiloxane). The PDMS was modified with different bulky hydrocarbon groups, like ethyl, propyl, octyl, and phenyl in the side chain as well as in the backbone chain. They observed that as the bulkiness of the substitution group increases the glass transition temperature of the polymer increases, which shows that the polymer loses its flexibility and the intersegmental backbone chain mobility is hindered. With the substitution of increasingly bulkier hydrocarbon functional groups, like ethyl, propyl, octyl, and phenyl groups in the side chain replacing the pendant methyl groups the permeability value for He, O₂, CO₂, and CH₄ were found to decrease markedly compared to the unsubstituted PDMS. For example the permeability value decreases for oxygen gas from 933 Barrer (unsubstituted PDMS) to 312 Barrer for ethyl substituted, 383 Barrer for propyl substituted, 190 Barrer for octyl substituted, and 32 Barrer for phenyl substituted, and similarly for CO₂ gas the permeability changes from 4553 to 339 Barrer. The selectivity value for O₂/N₂ improved from 2.0 to 3.1 with the increasingly bulky substitution.

In a similar manner they observed that the permeability value decreased with the substitution of different alkyl groups, like ethyl, hexyl, octyl, and phenyl groups in the backbone chain of PDMS for He, O₂, CO₂, and CH₄ gases. The permeability value for oxygen decreases from 933 to 11 Barrer and for CO₂ from 4553 to 64 barrer. The selectivity value was improved from 2.0 - 3.3 for O₂/N₂ gas mixture.

A siloxane containing polyamide was first reported by Speck who described that introduction of organosiloxane group into the polyamide backbone led to the increase of flexibility of the polymer chain. Polysiloxane containing amide group was prepared by various researchers. Kovacs et al. have investigated aromatic polyamides containing silyl moieties in the polymer backbone to obtain processable polymers which were stable to thermooxidation.

Takeo et al. have prepared multiblock copolymers (Scheme 1) containing PDMS and aromatic polyamide using 3,4-diaminodiphenyl ether, isophthaloyl chloride, and amino propyl terminated PDMS. The amount of PDMS in the copolymer was varied from 26 to 75 wt per cent. The prepared copolymer was cast into transparent films using N.N'-dimethylacetamide solutions. The oxygen and nitrogen permeability values for these polymeric membranes were found to increase with the increase in siloxane content. For 75 wt per cent of siloxane in the copolymer the oxygen permeability was shown to be 224 barrer and α (O₂/N₂) = 2.3, whereas for 46 wt per cent of siloxane in the copolymer the oxygen permeability was found to be 41 Barrer and α (O₂/N₂)

### Table 3—Molecular sieving diameter

<table>
<thead>
<tr>
<th>Molecule</th>
<th>He</th>
<th>H₂</th>
<th>NO</th>
<th>CO₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CO</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieving diameter (Å)</td>
<td>2.6</td>
<td>2.89</td>
<td>3.17</td>
<td>3.3</td>
<td>3.4</td>
<td>3.46</td>
<td>3.64</td>
<td>3.76</td>
<td>3.8</td>
<td>3.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

![Scheme 1](image-url)
= 2.4. The introduction of bulky and rigid amide group inhibits the local segmental motion and decrease the permeability value with a slight increase in the selectivity value.

Kiyotsukuri et al. have synthesized siloxane containing aliphatic polyamides by melt polycondensation of amino propyl terminated tetramethyldisiloxane with dicarboxylic acid having various chain length (HOOC-(CH₂)₉-COOH, where \( n = 1 \) to 10 (Scheme 2) and studied its permeation properties for oxygen and nitrogen gases. The permeability value for oxygen and nitrogen gas was found to decrease as the chain length of dicarboxylic acid increases, for oxygen (20.4 Barrer) and nitrogen (9.15 Barrer) and the selectivity value was found to be high (\( \alpha \) value for \( O_2/N_2 = 2.7 \) for \( n = 6 \) and low (\( \alpha \) value for \( O_2/N_2 = 2.4 \) for \( n = 12 \). As expected the selectivity increases as the chain segmental motion decrease due to the substitution of bulky groups which hinder the backbone mobility. When the chain length becomes too long as in the case of \( n = 12 \) the inhibition to its backbone mobility decreases which may lead to decrease in mobility selectivity and hence the selectivity would have decreased. The magnitude of permeability value is high in the case of siloxane containing aromatic polyamide group compared to the aliphatic polyamide group and this increase may be attributed to the packing inhibition of bulky groups which may lead to larger free volume and hence increase in permeability value.

Polymides generally have rigid chain structure, resulting in low gas permeability. The rigidity of the polymer chain reduces the segmental motion of the chain and plays a role as a good barrier against gas transport with increase in diffusion selectivity. To overcome the limit for use as materials for gas separation, many copolymers with flexible segments, such as siloxane and ether units were prepared. Incorporation of siloxane unit to polymides makes it possible to increase the solubility and processability. Several kinds of synthetic methods to incorporate siloxane groups into the polyimides have been achieved by various researchers.

Robeson et al. synthesized poly(imide-siloxane) membrane from pyromellitidianhydrides, methylene diamines and 1,3-bis(3-amino propyl) tetramethyl disiloxane by polycondensation reaction. The permeability value for oxygen and nitrogen gas for these membrane was found to be 7.5 and 3.41 Barrer, respectively. The separation factor, \( \alpha \) for \( O_2/N_2 \) gas mixture was found to be 2.2.

Bott et al. have synthesized poly(amide-siloxane) membrane by the polycondensation reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydrides and 1,3-bis(3-amino propyl) tetramethyl disiloxane. The presence of bulky rigid group is expected to decrease the segmental motion and hence decrease the permeability value. As expected the permeability value for oxygen and nitrogen gas for this membrane was found to be very low, 1.1 and 0.26, respectively. However the mobility selectivity was greatly enhanced and the separation factor \( \alpha \) for \( O_2/N_2 \) gases was found to be very high, \( i.e., 4.3 \).

Arnold et al. have synthesized poly(imide-siloxane) copolymers by poly condensation reaction of 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydrides, n-phenylenediamine and amine terminated PDMS. The permeability value for oxygen and nitrogen gas for this membrane was found to be 43.4 and 18.87 Barrer, respectively. The separation factor \( \alpha(O_2/N_2) \) was found to be in the range of 2.3. The introduction of bulky phenyl group may inhibit the chain packing which may be the reason for the high permeability value in this membrane.

A similar type of membrane was prepared by Chen et al. They have synthesized poly(siloxane-imide) copolymer using pyromellitidianhydrides (PMDA), 4,4'-oxydianiline (ODA) and amine terminated polydimethylsiloxane. Effect of PDMS content on the membrane morphology was studied, using X-ray diffraction technique. Both permeability value and diffusivity value were found to increase with increase in the PDMS content.

Polotskaya et al. has synthesized polysiloxane-polyimide copolymers optionally containing polyketone, polyether, fluoroalkyl, and polythioether groups. The polymers were synthesized by two step condensation procedure of aromatic dianhydrides with \( \gamma \)-amino propyl bis-terminated oligosiloxanes and allyl aromatic diamines, followed by cyclization of the formed polyamic acids. The oxygen and nitrogen permeability of these membranes were found to be high and the separation factor for oxygen and nitrogen were found to be around 2.
Yamada et al.\textsuperscript{80} synthesized siloxane containing polyimide membranes with various chemical structure and siloxane content for thermally stable gas separation membrane. The dependence of permeability and permselectivity on the siloxane content as well as the chemical structure of the polyimide was studied. They found that the permeability value of gases like oxygen, nitrogen, carbon dioxide, and methane increases with the siloxane content, while the permselectivity decreases.

Monique et al.\textsuperscript{81} synthesized hybrid polyimide-siloxane containing different proportion of silica by polycondensation of pyromellitic dianhydrides, amino silane (aminopropyl trimethoxysilane and aminopropyl methyl dimethoxysilane) and tetra- methylxysilane. The materials were characterized by TGA, IR, and \textsuperscript{29}Si-NMR techniques. Gas permeation measurements were studied at various temperatures for H\textsubscript{2}, CO\textsubscript{2}, and N\textsubscript{2}. It was found that the permeability of the two materials, prepared with two different amino silane, vary with the silane content and the nature of the amino silane. The gas transport was found to be thermally activated and the activation energy value vary with the silane content of the material.

Siloxanes containing both amide and imide groups were found to have excellent permeability value compared to the polyimide polymers containing either amide or imide group alone. Lee et al.\textsuperscript{82} synthesized polyamide-imide branched siloxane membranes (Scheme 3) from 4,4’-hexafluoroisopropylidene) diphthalic anhydride (6FDA), p,p’-oxydiamiline (ODA) and aminopropyl-terminated oligomeric dimethylsiloxane (ODMS) using N-methyl pyrrolidinone (NMP) and tetrahydrofuran (THF) as a solvent. With this membrane they found the permeability value as 456 Barer for oxygen gas and as 231 barer for nitrogen gas at 25°C. The selectivity value towards oxygen and nitrogen (\(\alpha\) for O\textsubscript{2}/N\textsubscript{2}) gas with this membrane was found to be 2.1. This membrane was found to have high permeability value compared to the membranes prepared from the poly(amide-siloxane) or poly(amide-imide-siloxane) membranes. This difference in permeability value can be attributed to decrease in packing density due to the incorporation of ODMS as a side chain into the backbone of polyamide-imide group, leading to more free volume within the polymer matrix.

Higashi et al.\textsuperscript{83} synthesized poly(amide-imide) containing siloxane membrane from trimellitic anhydride chloride, 4,4’-oxydianiline and amine terminated oligomeric dimethylsiloxane. The permeability value for oxygen and nitrogen gas for this membrane was found to be 120 and 51.72 Barrer, respectively. The selectivity value was found to be 2.3.

Stern et al.\textsuperscript{60} observed that the incorporation of phenyl group in the siloxane unit increased the selectivity value for O\textsubscript{2}/N\textsubscript{2}. Kawakami et al.\textsuperscript{84} synthesized p-oligo organosiloxane substituted styrene (Scheme 4) using p-vinyl phenyl magnesium chloride and substituted chlorosilanes. These polymers were obtained by free radical polymerization and cast into thin films using THF. They found that the polymer with less siloxane content give a brittle film and higher siloxane content were waxy and lacked film forming property. The polymer with \(n = 1\) form tough film and showed good result for oxygen with permeability value of 100 Barrer and considerably high separation factor of 2.8 for oxygen and nitrogen gas pairs.

Kawakami et al.\textsuperscript{84} have also studied the effect of the permeation behaviour of oligosiloxane substituents (oligodimethyl siloxane of branched structure, cyclic structure and those having different alkyl group at o-terminal) on polystyrene by introducing these groups at the p-position of the polystyrene. They found that the structure of p-oligosiloxane substituents had greater effect not only on glass transition temperature of the polymer but also on the oxygen permeation behaviour through the polymer film. In most of the substituted polymers, it was observed that there is increase in permeability value and it may due to increase in diffusion coefficient. It was also observed that introduction of cyclic structure into oligodimethyl siloxane structures results in decrease in permeability coefficient of the polymer compared with those having same number of silicon atoms in the linear substituents. The
introduction of bulky groups like phenyl, triphenyl, substituted siloxanes at the C-terminal lowers the permeability coefficient of oxygen irrespective of the higher concentration of siloxane linkage in the polymers. Replacing the styrene unit with vinyl and benzyl type substituents the permeability coefficient was found to increase compared with the styrene type polymer having the same silicon atoms. The permeability value for oxygen gas in the oligosiloxane substituted polystyrene ranges from 47-71 Barrer, whereas for nitrogen gas it ranges from 5.6-25 Barrer. The separation factor for oxygen and nitrogen ranges from 2.7-4.0.

It was also concluded that the structure of the side chain is very important in determining the oxygen permeability coefficient through the polymer films. The trimethyl siloxyl group, especially at the terminal place plays an essential role in enhancing the permeability coefficient by enhancing the diffusion coefficient. The spacer oligodimethyl siloxane or methylene linkage is important to give the terminal trimethyl siloxyl group maximum mobility. Replacement of methyl group of terminal trimethyl siloxyl group by other group lowers the mobility of the terminal by substituted siloxyl group, resulting in lower permeability coefficient of oxygen through the polymer film.

Various researchers have described a synthetic method to prepare polysiloxane/polystyrene copolymers. They also showed that these polymers could be modified by the incorporation of the highly stericly demanding tris (trimethyl silyl) methyl substituents (Me, Si), C. The DSC analysis showed that the modification increases the rigidity of the polymers. The effect is especially dramatic in the case of silyl substituted polysiloxane copolymer. The steric bulk group, tris(trimethyl silyl)methyl in polysiloxane polymer renders 8 per cent of Si-H bonds in poly(methyl hydro siloxane), which is one of the reactant, unreactive towards the hydroisilylation process. The SiH bonds of the resultant copolymer can be utilized for crosslinking of the linear polysiloxane to prepare membranes.

Brown and Price have synthesized PDMS - polystyrene block copolymers. This synthesis involves chloromethyl terminated polysiloxane as initiator for atom transfer radical polymerization. The copolymer formed was characterized by NMR. The thermal properties of these polymers were studied by DSC analysis.

Ashworth et al. synthesized polysiloxane containing ester functionalities by the platinum catalysed hydrosilylation reaction. They have incorporated different ester functionalities -(CH2)-COOR, (R = -Me, -CF3, -Et, Pr and -CH2COME), -(CH2)3-CHMeCO2Et, -(CH2)2-CH(MeCO2Me), -(CH2)2-CH(MeCO2Et), -(CH2)2CO2CH=CHCO2CH=CH2 and -(CH2)2CO2C6H5CO2CH=CH2 into the poly methyl hydrogen siloxane (Me2SiO-(Me3Si(H)O)n-SiMe3) under the anhydrous condition. They found that the amount of catalyst and temperature play a significant role in the product formation. The products were well characterized by IR and 1H and 13C NMR techniques.

Ashworth et al. also synthesized a series of polyorganosiloxane membranes functionalized to various degrees of ester group by platinum catalysed hydrosilylation reaction, Me2SiO(Me3Si(H)O)n[Me3Si((CH2)2COOMe)O]3SiMe3, (Scheme 5). Catalysed crosslinking of the remaining Si-H unit in the functionalized polymer with α, ω-dihydroxy poly(dimethylsiloxane) lead to the formation of membrane. The Tg value of these polymers was found to be around -120 °C. The permeabilities for CO2, CH4, O2, and N2 show a slight decrease with increase in ester functionality. The solubility value for CH4, O2, and N2 remains constant and that for CO2 was found to increase with increasing ester functionality. The selectivity of CO2 over CH4 was found to increase with increasing ester functionality as a result of improved solubility selectivity. The diffusivity selectivity remained virtually unchanged. In the case of O2 and N2 the selectivity for O2 over N2 slightly decreased with greater ester functionality due to the reduction in the mobility selectivity.

Tronc et al. synthesized tailor-made polysiloxanes with anchoring groups by polycondensation using hydrosilylation reaction. They prepared copolymers of dimethyl siloxane segments of different lengths regularly separated by one
biphenol A unit. They achieved this by performing
hydrosilylation of 2,2'-diallylbiphenol-A with
hydride terminated polydimethylsiloxanes in the
presence of Pt catalyst. The influence of several
factors including the control of the [Si-H]/[double
bond] ratio and the protection of -OH groups on the
molecular weight distribution of the polymer
was reported. Side reaction, such as isomerization of the
double bond and O-silylation was studied by 1H and
29Si NMR techniques.

Conclusions
Functionalization of poly(dimethylsiloxane)
with different organic groups affect the permeability
and selectivity value for oxygen and nitrogen gas has
been reviewed. From the results, one can find that the
permeability and selectivity result for similar sized
and less condensable penetrants, like oxygen and
nitrogen gas mixture, highly depends on the mobility
selectivity. The mobility selectivity can be increased
by introducing bulky substituents which hinder the
backbone mobility and decrease the intersegmental
motion but the permeability value decrease. Solubility
selectivity plays a major role for highly condensable
penetrants like, CO2 and CH4 and it can be increased
by substitution of polar groups in the polymer chain.

Current and Future Industrial Applications for
Membrane Technology
Petrochemical and gas producers, as well as
environmental service industries recognize the
advantages of applying membrane technology to
process operations. Membrane-based gas separations
have already made significant commercial
contributions in various industrial applications, such
as the production of nitrogen enriched air for inert gas
blanketing applications; CO2 removal in natural gas
treatment; hydrogen recovery during industrial
process operations; and oxygen enrichment. For example, stringent SO2 removal from smelter gas
streams, H2S, and water removal from natural gas,
and separations of hydrocarbon and chloro-
fluorocarbon vapours from air. It was recognized
that the next generation of gas separation membranes will
not only require heightened selectivity to improve the
quality of the separations, but also improved
permeability to permit increased production levels for
industrial requirements.

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