CHAPTER 11

PERMEATION OF NITROGEN AND OXYGEN THROUGH SBR, NR AND SBR/NR BLEND MEMBRANES

The results of this chapter have been communicated to Journal of Polymer Engineering Science
Membrane technology for gas separation has now emerged as a viable alternative to conventional technologies such as cryogenics and pressure swing adsorption. Further, growth of the technology depends upon the development of membrane with high selectivity and high permeability. A large number of gas permeability data has been reported for many kinds of conventional polymers in the literature.\textsuperscript{1,2} With the growing interest in gas separation membranes, the study of gas transport properties of various polymers, including engineering plastics and novel polymers, has been accelerated during the last decade. Some examples are the studies by Toi \textit{et al.}\textsuperscript{3} and Chern \textit{et al.}\textsuperscript{4} for poly(phenylene oxides), Chiou \textit{et al.}\textsuperscript{5} for polysulfone and polyethersulfone, Min and Paul\textsuperscript{6} for poly(methylmethacrylates), Walker and Koros\textsuperscript{7} for polypyrrole and Ichiraku \textit{et al.}\textsuperscript{8} for poly(1-trimethyl-1-silyl-1-propyne).

Recently Lai and co-workers\textsuperscript{9} reported studies on the sorption and transport mechanism of gases in polycarbonate membranes. Cobalt acetyl acetone [Co(acac)\textsubscript{3}] was added into a polycarbonate membrane to enhance its oxygen solubility. They found that the oxygen solubility decreased sharply as pressure increased, especially at low pressure region. Ruaan \textit{et al.}\textsuperscript{10} investigated the oxygen/nitrogen separation by polycarbonate/Co (Sal Pr) complex membranes. It was found that both oxygen permeability and oxygen/nitrogen selectivity increased when only 3 wt % Co (Sal Pr) was added.
The polymer blending is an important means of obtaining new materials for membrane preparations.\textsuperscript{11-13} Compared to copolymers, mixture of these polymers often have better physical properties which can be varied by adjusting the composition of the blend. Permeation properties are sensitive to changes in membrane structure such as crystallinity, crosslinking, and phase morphology.

In the previous chapters, the transport of liquids and vapours through styrene-butadiene rubber, natural rubber and their blends has been reported. It is equally important to study the gas permeation behaviour of these membranes for various applications. The gas permeation characteristics of styrene-butadiene rubber vulcanised with different crosslinking systems and styrene-butadiene rubber and natural rubber blends with respect to nature of crosslinks and blend ratio are discussed here.

11.1. Results and discussion

11.1.1 SBR membranes

The oxygen and nitrogen permeabilities for SBR membranes vulcanised by different crosslinking systems are shown in Table 11.1. As apparent from Table 11.1 that SBR vulcanised with EV systems exhibit high gas permeability and those with DCP systems exhibit low permeability. SBR membranes vulcanised with CV and mixed systems exhibit intermediate values. The structure of crosslinks formed during vulcanisation process is already discussed (Figure 9.7). Depending on the flexibility of crosslinks the gas permeability would be in the order CV > mixed > EV > DCP instead of the observed behaviour EV > mixed > CV > DCP. In order to establish the observed behaviour, the crosslink density of the SBR membranes were determined and are also given in Table 11.1.
Table 11.1. Permeability and Crosslink density values (SBR).

<table>
<thead>
<tr>
<th>Systems</th>
<th>$P \times 10^8$ (cm$^3$ cm$^{-2}$s cm Hg)</th>
<th>$n_1 \times 10^4$ (mol/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_2$</td>
<td>$N_2$</td>
</tr>
<tr>
<td>EV</td>
<td>6.95</td>
<td>1.92</td>
</tr>
<tr>
<td>Mixed</td>
<td>6.58</td>
<td>1.78</td>
</tr>
<tr>
<td>CV</td>
<td>6.12</td>
<td>1.47</td>
</tr>
<tr>
<td>DCP</td>
<td>6.02</td>
<td>1.09</td>
</tr>
</tbody>
</table>

It is very clear from the table that DCP membrane with the highest crosslink density exhibits the lowest gas permeability and EV membrane with the lowest crosslink density exhibits the highest gas permeability. As the number of crosslinks per unit volume of the polymer increases, it is very difficult for the gas molecules to pass through the tightly cross linked system. Therefore, the crosslink density and partly the nature of crosslinks influence the gas permeation behaviour.

11.1.1.1 $O_2/N_2$ selectivity of SBR membranes

The variation of $O_2/N_2$ selectivity with crosslinking systems is given in Figure 11.1. It is clear from the figure that peroxide membrane exhibits high selectivity and the efficiently vulcanised membrane exhibits the low selectivity. CV and mixed systems exhibit intermediate selectivity values. The sample which exhibits high permeability shows only low selectivity and vice versa. The observed selectivity is also related to the crosslink density of the samples (Table 11.1). The relation between the oxygen-to-nitrogen selectivity and oxygen permeability is given in Figure 11.2. In general, an approximately linear relation with negative slope exists between the oxygen-to-nitrogen selectivity and oxygen permeability has been reported. In this case also an approximately linear relationship was
observed. Also, it is reported that gas permeability usually follows the solution-diffusion mechanism for many polymer systems. Using SBR membranes, if gas permeability follows the solution-diffusion mechanism, the glass transition temperature of the polymer membrane and diffusion constant are the important factors controlling the process, and an approximately linear relation should exist between them. The relation between glass transition temperature of the differently crosslinked SBR and oxygen permeability is shown in Figure 11.3.

**Figure 11.1.** Variation of $O_2/N_2$ selectivity with crosslinking systems in SBR membranes.

**Figure 11.2.** Variation of $O_2/N_2$ selectivity with oxygen permeability.
As gas molecules pass through the molecules of the polymer membrane, the rate of permeation is higher if the molecular structure is not rigid or the polymer has a high free volume, i.e. the polymer having lower glass transition temperature has higher gas permeabilities. As given in figure, an approximately linear relation is found between glass transition temperature and oxygen permeabilities. As the $T_g$ decreases sharply from peroxide to EV, the gas permeability increases.

11.1.2 SBR/NR blends

The $O_2$ and $N_2$ permeability values of SBR/NR blends vulcanised with different vulcanising systems are given Table 11.2. Both oxygen and nitrogen permeabilities decrease from EV to DCP as in the case of SBR homopolymer. The
nature of crosslinks formed between rubber chains is identical to that of SBR. Based on the flexibility of crosslinks we can only expect a high permeability for CV sample rather than EV. The crosslink density given in Table 11.2 is in agreement with this observation. The DCP sample with highest crosslink density exhibits the lowest gas permeability, whereas the EV sample having the lowest crosslink density exhibits the highest gas permeability.

Table 11.2. Permeability and crosslink density values (SBR/NR blends).

<table>
<thead>
<tr>
<th>Systems</th>
<th>$P \times 10^8$ (cm$^3$ cm$^2$ s cm Hg)</th>
<th>$n_1 \times 10^4$ (mol/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_2$</td>
<td>$N_2$</td>
</tr>
<tr>
<td>EV</td>
<td>16.00</td>
<td>6.93</td>
</tr>
<tr>
<td>Mixed</td>
<td>15.43</td>
<td>6.39</td>
</tr>
<tr>
<td>CV</td>
<td>15.3</td>
<td>6.09</td>
</tr>
<tr>
<td>DCP</td>
<td>14.57</td>
<td>5.10</td>
</tr>
</tbody>
</table>

The oxygen-to-nitrogen selectivity of SBR/NR blend membranes vulcanised by different crosslinking systems is shown in Figure 11.4. The selectivity is maximum for DCP membrane and minimum for EV membrane. CV and mixed membranes have intermediate values. This behaviour is truly related to the crosslink density as in the case of SBR membrane. The variation of oxygen-to-nitrogen selectivity to oxygen permeability is shown in Figure 11.5. An approximately linear relation was observed between them.
Figure 11.4. Variation of $O_2/N_2$ selectivity of SBR/NR blends with different crosslinking systems.

Figure 11.5. Variation of $O_2/N_2$ selectivity with oxygen permeability of SBR/NR blends.
11.1.3 Effect of blend composition on pure gas permeability

The permeability coefficients of SBR, NR and SBR/NR blends to O$_2$ and N$_2$ at 25°C are shown in Figure 11.6. In all cases, gas permeability increases with increasing NR concentration. The oxygen and nitrogen permeability slowly increase with increase of volume fraction of NR (up to 0.3) and then sharply increase. This behaviour is associated with the blend morphology. As seen from Figure 8.2, in N$_{30}$ the highly permeating NR component forms the dispersed phase in the continuous SBR matrix. This dispersed/matrix heterophase morphology makes a tortuous path for the permeation of gas molecules. In N$_{50}$ the dispersed NR becomes continuous and thereby a sharp increase in gas permeability. The relatively high permeability of N$_{70}$ may also be due to the co-continuous morphology.

![Graph showing variation of gas permeability with volume fraction of NR.](image)

**Figure 11.6.** Variation of gas permeability with volume fraction of NR.
It is also seen from the Figure 11.6 that oxygen exhibits higher permeability compared to nitrogen. With increasing NR concentration permeability to oxygen increases more rapidly compared to permeability to nitrogen. The permeabilities of polymer are to be a very sensitive function of penetrant size. Thus the increase in permeability coefficient is more for oxygen compared to nitrogen as the kinetic diameter of oxygen is less than that of the nitrogen.

### 11.1.4 Comparison of pure gas permeability of SBR/NR blends with models for permeation in heterogeneous media

The experimental gas permeabilities in SBR/NR blends are compared with several theoretical models of permeation in heterogeneous blends\(^{14,15}\). Mixing rules for predicting permeability of gases in homogeneous and heterogeneous blends and copolymers have been developed from a simple free volume model and from the activated state theory of transport which reduces to\(^{15}\)

\[
\log P_{\text{blend}} = \phi_1 \log P_1 + \phi_2 \log P_2 \tag{11.1}
\]

where \(P_{\text{blend}}\) is the gas permeability of blend. \(\phi_1\) and \(\phi_2\) are the volume fractions of polymer 1 and 2 in the blend and \(P_1\) and \(P_2\) are the permeabilities of pure polymer 1 and 2, respectively. Figure 11.7 represents the experimental and theoretical oxygen permeabilities of SBR/NR blends. The difference between the two establishes the heterophase nature of the blend. There is a marked positive deviation at higher concentration of NR in the blend. This deviation is due to the co-continuous nature of \(N_{50}\) and \(N_{70}\) compositions.
Figure 11.7. Experimental and theoretical gas permeabilities of SBR/NR blends.

Two theoretical models viz. Maxwell and Bruggeman models were used to describe the transport properties of SBR/NR blends and to discuss on the heterostructure of the phase separated SBR/NR blends. These models also provide insights into the structure of the heterophase SBR/NR blends.

The Maxwell model was originally applied to permeation in systems in which the dispersed phase consisted of a low fraction of spherical particles. According to Petropoulos, Maxwell Model is, in fact, valid over the whole composition range for dispersion of isometric particles of such shape and mode of packing that the interparticle gaps are uniformly maximised. The Bruggeman model corresponds to a random packing of dispersed, isometric particles. When the low permeability component is the continuous phase, the Maxwell model gives the lower estimates of permeability than the Bruggeman model. When the high permeability component is the continuous phase the Maxwell model predicts higher
permeability coefficients than the Bruggeman model. The Maxwell and Bruggeman models are expressed in mathematical forms as follows.

**Maxwell**

\[
P_{\text{blend}} = P_c \left[ 1 + \frac{3\phi_d}{P_d/P_c + 2} - \phi_d \right] \tag{11.2}
\]

**Bruggeman**

\[
P_{\text{blend}} = P_c \left( \frac{P_d / P_c - P_{\text{blend}} / P_c}{1 - \phi_d} \right)^3 \tag{11.3}
\]

where \( P_{\text{blend}} \) is the permeability of the blend; \( P_c \), the permeability of the continuous phase; \( P_d \), the permeability of the dispersed phase; and \( \phi_d \), the volume fraction of the dispersed phase. The volume fraction of NR in the blend was estimated from

\[
\phi_{\text{NR}} = \frac{W_{\text{NR}} \rho_{\text{blend}}}{\rho_{\text{NR}}} \tag{11.4}
\]

where \( W_{\text{NR}} \) and \( \rho_{\text{NR}} \) are respectively the weight fraction and density of NR in the blend. The blend density, \( \rho_{\text{blend}} \) was calculated from

\[
\rho_{\text{blend}} = \frac{1}{W_{\text{NR}}/\rho_{\text{NR}} + W_{\text{SBR}}/\rho_{\text{SBR}}} \tag{11.5}
\]

where \( W_{\text{SBR}} \) and \( \rho_{\text{SBR}} \) are the weight fraction and density of SBR in the blend respectively. Using pure component permeability values for each penetrant in SBR and NR, the Maxwell and Bruggeman models predict the dependence of permeability on blend composition. A comparison of blend permeability values predicted by these models and experimental data is shown in Figure 11.8 for oxygen. Nitrogen result was qualitatively similar to the behaviour of \( O_2 \). The model predictions are shown for both SBR and NR as the continuous phase. As expected, the Maxwell model predicts lower blend permeabilities than the Bruggeman model when SBR is treated as the continuous phase.
In SBR/NR blend with 0.3 volume fraction of NR, the permeability data is close to Maxwell model with SBR is the continuous phase. Thus in this blend the highly permeating NR forms the dispersed phase in the continuous SBR matrix. There is an inflection point between 0.3 and 0.5 volume fractions and this indicate a phase inversion. At 0.5 and 0.7 volume fraction of NR, the permeability of the blend is close to Maxwell model with NR is the continuous phase.

11.1.5 Effect of blend composition on oxygen to nitrogen selectivity

Pure gas oxygen/nitrogen selectivity of SBR/NR blends is given in Figure 11.9. Oxygen permeability increases as the content of NR in the blend increases (Figure 11.6). In contrast, the O₂/N₂ selectivity decreases sharply with increasing NR concentration in the blend.
The change in selectivity with blend composition could be related to phase inversion occurring over a narrow concentration range as is evident from morphology of the blends. NR is more permeable than SBR to $N_2$ and $O_2$. Thus for theoretical models, if NR is the continuous phase, then $P_{d}/P_{c} < 1$; if SBR is the continuous phase, then $P_{d}/P_{c} > 1$. In either of these limits, the Maxwell model yields the following prediction for blend selectivity.

$$\alpha'_{A,B} = \frac{P_{c,A}}{P_{c,B}}$$  \hspace{1cm} (11.6)

where $\alpha'_{A,B}$ is the ratio of permeability of penetrants $A$ and $B$ in the blend. The permeabilities of the continuous phase to penetrants $A$ and $B$ are $P_{c,A}$ and $P_{c,B}$ respectively. According to the Maxwell model, the blend selectivity should be the selectivity of the continuous phase, and selectivity should be independent of blend
composition as long as phase inversion does not occur. In blends with NR content less than 30 wt % of NR, SBR is the continuous phase. NR is the continuous phase for blends with NR concentrations greater than 70 wt %. Between 30 and 70 wt % of NR, the data suggest a co-continuous structure with both components being continuous. At concentrations above 70 wt % of NR, the blend selectivity is essentially that of NR. These predictions are consistent with the results obtained from morphology studies. This interpretation of the SBR/NR blend results is substantiated by the earlier work of Ranby and co-workers. The gas transport properties in blends of poly(vinyl chloride) (PVC) and poly(ethylene-co-vinyl acetate) (PEVA) were determined in their studies. The vinyl acetate content in PEVA was varied to prepare either compatible blends (45% VA) or phase separated blends (65% VA). For phase separated blends a sharp decrease in selectivity occurs as the PEVA concentration in the blend increases from approximately 20%. At higher PEVA contents, the selectivity of the blend is essentially constant and equal to the selectivity in pure PEVA. At PEVA contents below 10%, the selectivity is similar to that of pure PVC. These blends undergo phase inversion, from PVC continuous to PEVA continuous. These results suggest that the sharp change in selectivity observed in this study with SBR/NR blends may be associated with phase inversion in the blend.

11.2. References


