Chapter 7

Transport of Chlorinated Hydrocarbon Vapours through Natural Rubber, Epoxidised Natural Rubber and their Blends

Results of this chapter have been communicated for publication in Journal of Polymer Science, Polymer Letters
The transport of a condensable vapour through a dense membrane consecutive to an activity gradient is usually referred to as vapour permeation process. Vapour permeation offers the unique feature, from a fundamental point of view of studying the transport process of a single permeant through a dense membrane, under various upstream concentrations (activities). Such a characteristic can by no means be obtained by liquid permeation, where the modification of the upstream activity of a component can only be achieved by adding another component to the mixture. The activity of both components is modified in this case in compliance with the Gibbs-Duhem relation, which complicates the transport analysis. In the case of pure solvent vapour permeation, upstream activity can be easily calculated, provided upstream pressure is precisely monitored.

Apart from this fundamental advantages a study of solvent vapour permeation offers direct practical conclusion for the understanding and rational design of volatile organic components (VOC) vapour recovery from contaminated air stream. For VOC vapour recovery as well as organics extraction from aqueous stream by pervaporation, a membrane material showing high organic vapour permeabilities, but low air and water permeabilities is required in order to set up a competitive process.

Equilibrium sorption of a vapour has been used for the thermodynamic characterisation of polymer blend. Analysis of equilibrium sorption of a vapour
by the blend can provide information regarding polymer-polymer interaction. The usual technique to investigate the morphology of immiscible polymer blends is scanning electron microscopy applied to the surface of cryofracture. However, that technique gives a picture of only a minute portion of the sample that is sometimes non-representative of the bulk of the material. Moreover, from a two dimensional picture it is not easy to estimate when phase inversion occurs as a function of composition and when the level of phase co-continuity reaches a maximum.

This chapter intends to examine the influence of the sorption and diffusion steps in the overall permeation flux of organic vapours. Further, permeation results have been used to compliment the observations from scanning electron microscopy.

7.1 Results and discussion

Permeation through polymer film is a result of two distinct processes, solubility, which is a thermodynamic quantity and diffusion a kinetic one.\(^7\)\(^{-10}\)

\[
P = D \times S\]

(7.1)

where \(P\), \(D\) and \(S\) are the permeability, diffusion and solubility coefficients. Permeability through a polymeric film depends on many factors; (1) external (temperature, pressure, concentration, humidity etc.); (2) penetrant (solubility, molecular shape, weight etc.) and (3) polymer.\(^{11\text{-}13}\) A detailed analysis of the transport process of a single permeant can thus be achieved provided sorption and either diffusion or permeation can be studied independently. However, it has been suggested that effective diffusion coefficients obtained from permeability and sorption measurements are more realistic for a correct transport description.\(^{14}\)

At a given temperature, pressure and concentration, permeability through the polymer depends on solubility of the solvent molecule into the polymer membrane and the diffusivity in it. The solubility of the penetrant generally becomes high when the difference in the solubility parameter between the polymer and the penetrant is small.\(^{15\text{-}16}\) However, when the polymer has a compact network
structure, diffusivity of a penetrant through the polymer membrane tend to decrease.\textsuperscript{17} Description of diffusion mechanism in rubbery polymers is essentially concerned with the ability of the polymer to continually provide opportunities for the permeant to progress in the form of randomly generated voids.\textsuperscript{18}

7.1.1 Effect of epoxidation

Analysis of the permeation coefficient values show that, the permeability coefficient decreases with epoxidation where as the sorption constants increase with epoxidation (Figure 7.1). The increase in sorption constants for ENR-25 and ENR-50 can be explained by the difference in solubility parameter between the polymer and solvent. These values given in Table 7.1 explain the increased sorption constant values with epoxidation.

![Figure 7.1. Effect of epoxidation on the permeation and sorption coefficients.](image-url)
The decrease in permeation coefficient values can be explained by the decreased diffusivity of the permeant molecules through the polymer membrane. Figure 7.2 shows the variation of permeation and diffusion coefficients with epoxidation.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NR</th>
<th>ENR-25</th>
<th>ENR-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>3.6</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>2.8</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>CCl₄</td>
<td>1.4</td>
<td>0.4</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

*Table 7.1. Solubility parameter difference between polymer and solvent (Jm⁻³)¹/².*

**Figure 7.2.** Effect of epoxidation on the permeation and diffusion coefficients.
It is seen that diffusivity decreases with epoxidation. This is because of a more compact polymeric network structure in ENR. With epoxidation, Tg values increase (NR = -72°C, ENR-25 = -47°C, ENR-50 = -24°C). This increased Tg values suggest less polymeric chain mobility in ENR which decreases the diffusivity of penetrant molecules. Another factor to be considered is the increased gel content in ENR discussed in Section 3.1.2. The SEM observations given in Figure 3.7 confirm the gel phase in ENR. The gel phase hinders the mobility of the penetrant molecules with a consequent decrease in diffusion coefficient values.

7.1.2 Blend morphology

The morphologies of NR/ENR-25 and NR/ENR-50 blends are given in Figures 7.3 and 7.4.

**Figure 7.3.** SEM photographs of NR/ENR-25 blends: (a) 70/30, (b) 50/50 and (c) 30/70.
The tiny holes observed in the figure comes from the debonding of dispersed phase from the continuous phase. As already established by Roland and Bohm\textsuperscript{19} and Tokita\textsuperscript{20} that during mixing of rubber blends, the dispersed domains are deformed during the passage through the high shear regions of the mixing mill and under such condition the domains will undergo break up to form smaller particles or coalesce to form larger dispersed domains. In fact the final morphology is an equilibration between domain break up and coalescence. The SEM photograph show that in both NR/ENR-25 and NR/ENR-50 blends, at low volume fraction of ENR, well dispersed, almost spherical drops are observed. With the increase in volume fraction of the dispersed phase, individual particles coalesce and finally

Figure 7.4. SEM photographs of NR/ENR-50 blends: (a) 70/30, (b) 50/50 and (c) 30/70.
most particles become very elongated and tend to form a continuous phase. The size characteristics of the dispersed phase ($D_n, D_w, D_a$ and $D_v$) and its distribution (polydispersity index values) in the different blend compositions are presented in Tables 7.2 and 7.3. These are calculated using the equations.²¹

No. average diameter, $D_n = \frac{\sum N_i D_i}{\sum N_i}$ (7.2)

Weight average diameter, $D_w = \frac{\sum N_i D_i^2}{\sum N_i D_i}$ (7.3)

Surface area average diameter, $D_a = \sqrt[2]{\frac{\sum N_i D_i^2}{\sum N_i}}$ (7.4)

Volume average diameter, $D_v = \sqrt[3]{\frac{\sum N_i D_i^3}{\sum N_i}}$ (7.5)

where $N_i$ is the number of particles having a diameter $D_i$.

Table 7.2. Blend characteristics of NR/ENR-25.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>NR/ENR 70/30</th>
<th>NR/ENR 30/70</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_n$ (µm)</td>
<td>7.70</td>
<td>4.116</td>
</tr>
<tr>
<td>$D_w$ (µm)</td>
<td>11</td>
<td>5.32</td>
</tr>
<tr>
<td>$D_a$ (µm)</td>
<td>9.25</td>
<td>4.68</td>
</tr>
<tr>
<td>$D_v$ (µm)</td>
<td>10.725</td>
<td>5.38</td>
</tr>
<tr>
<td>PDI</td>
<td>1.43</td>
<td>1.29</td>
</tr>
</tbody>
</table>
Table 7.3. Blend characteristics of NR/ENR-50.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>NR/ENR 70/30</th>
<th>NR/ENR 30/70</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overline{D}_n$ (µm)</td>
<td>3.96</td>
<td>2.28</td>
</tr>
<tr>
<td>$\overline{D}_w$ (µm)</td>
<td>6.50</td>
<td>2.88</td>
</tr>
<tr>
<td>$\overline{D}_a$ (µm)</td>
<td>5.07</td>
<td>2.56</td>
</tr>
<tr>
<td>$\overline{D}_v$ (µm)</td>
<td>6.06</td>
<td>2.85</td>
</tr>
<tr>
<td>PDI</td>
<td>1.64</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Polydispersity index (PDI) which is a direct measure of size distribution of the dispersed phase is calculated as

$$PDI = \frac{\overline{D}_w}{\overline{D}_n} \quad (7.6)$$

It is clear from the table that $\overline{D}_n$, $\overline{D}_w$, $\overline{D}_a$ and $\overline{D}_v$ decrease as the composition changes from NR/ENR 70/30 to NR/ENR 30/70 for both NR/ENR-25 and NR/ENR-50 blends. NR/ENR 50/50 composition shows a co-continuous morphology. The PDI values show more uniform particle distribution for 30/70. The normal and the cumulative distribution curves of NR/ENR 70/30 and NR/ENR 30/70 composition of NR/ENR-25 and NR/ENR-50 are given in Figures 7.5 and 7.6.
Figure 7.5. Particle size distribution curves of NR/ENR-25 70/30 and 30/70 compositions.

Figure 7.6. Particle size distribution curves of NR/ENR-50 70/30 and 30/70 compositions.
Investigation of the permeability data in NR/ENR blends show an interesting trend. In both NR/ENR-25 and NR/ENR-50 blends, the sorption constants increase with volume fraction of ENR. This variation for NR/ENR-25 blends is given in Figure 7.7. NR/ENR-50 blends yield similar curves which are not given.

![Figure 7.7. Variation of permeation and sorption coefficients for NR/ENR-25 blends.](image)

The sorption constant which is a thermodynamic parameter depends on the solubility parameter difference between the polymer and the solvent. The solubility parameter difference between the polymer and the solvent is given in Tables 7.4 and 7.5. From the values given in tables it can be seen that the solubility parameter difference between the polymer and solvent decreases with increase in volume fraction of ENR. Thus the sorption constant is a minimum for NR, which increases
with volume fraction of ENR and reaches a maximum for ENR which is in accordance with the solubility parameter difference between the polymer and the solvent. However, the permeation coefficient values show a different trend. For both NR/ENR-25 and NR/ENR-50 blends, the 70/30 composition shows the lowest permeation coefficient values and 50/50 composition the highest. The permeation coefficient is a composite term which involves the thermodynamic sorption constant and the kinetic diffusion coefficient. Thus the variation in permeation coefficient values can be explained on the basis of the variation in diffusion coefficient values which is a kinetic parameter. This behaviour for NR/ENR-25 blends is given in Figure 7.8. NR/ENR-50 blends yield similar curves which are not given. Figure 7.8 shows the lowest diffusion coefficient values for the 70/30 composition and the highest for 50/50 composition.

Table 7.4. Solubility parameter difference between NR/ENR-25 blends and solvent (Jm\(^{-3}\))\(^{1/2}\).  

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NR</th>
<th>NR/ENR 70/30</th>
<th>NR/ENR 50/50</th>
<th>NR/ENR 30/70</th>
<th>ENR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>3.60</td>
<td>3.24</td>
<td>3.00</td>
<td>2.76</td>
<td>2.40</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>2.80</td>
<td>2.44</td>
<td>2.20</td>
<td>1.96</td>
<td>1.60</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>1.40</td>
<td>1.04</td>
<td>0.80</td>
<td>0.56</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 7.5. Solubility parameter difference between NR/ENR-50 blends and solvent (Jm\(^{-3}\))\(^{1/2}\).  

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NR</th>
<th>NR/ENR 70/30</th>
<th>NR/ENR 50/50</th>
<th>NR/ENR 30/70</th>
<th>ENR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>3.60</td>
<td>2.94</td>
<td>2.50</td>
<td>2.06</td>
<td>1.60</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>2.80</td>
<td>2.14</td>
<td>1.70</td>
<td>1.26</td>
<td>0.80</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>1.40</td>
<td>0.74</td>
<td>0.30</td>
<td>-0.14</td>
<td>-0.60</td>
</tr>
</tbody>
</table>
These observations result from the unique morphology of NR/ENR blends. From the SEM photographs it is seen that the 70/30 composition presents a heterogeneous dispersed phase morphology and the 50/50 composition gives a co-continuous morphology. The dispersed domains in the 70/30 composition offers a more tortuous path for the penetrants thereby reducing the diffusivity through the membrane which in turn results in the reduction in permeability coefficient. The co-continuous nature of the 50/50 composition offers a smooth passage for the penetrants through the membrane, thereby showing increased permeability. The permeability coefficient values of NR/ENR 30/70 composition explains the heterogeneous nature of the 30/70 composition. Thus by controlling the morphology one can dictate the transport phenomenon.
7.1.3 Investigation of the blend morphology

The permeability of immiscible polymer blends depends on their morphology. Two extreme situations can be considered corresponding to multilayers of the components either parallel or perpendicular to the direction of the permeant flux. With respect to that direction, they can be considered as fully continuous and fully discontinuous phase morphology, respectively. If the continuous phase is the more permeable, a parallel configuration represents the limiting behaviour. The permeability of such systems varies with the permeabilities $P_1$ and $P_2$ of the individual components and with their volume fraction $\phi_1$ and $\phi_2$ according to equation

$$ P = \phi_1 P_1 + \phi_2 P_2 $$

(7.7)

The series model serves as the limiting case when the dispersed phase exhibits the greater permeability. The permeability in such systems is given by the equation

$$ \frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2} $$

(7.8)

A plot of permeability vs. volume fraction shows an upward concavity for parallel and downward concavity for series configuration. In polymer blends, with more complex morphologies, a change of concavity is also expected to occur with phase inversion when a dispersed phase becomes continuous and vice versa. Robesson et al.\textsuperscript{22} have combined these extremes to obtain an expression for the permeability given by

$$ P = X_a P_1 \left[ \frac{P_2 + 2P_1 - \phi_2(P_1 - P_2)}{P_2 + 2P_1 + \phi_2(P_1 - P_2)} \right] + X_b P_2 \left[ \frac{P_1 + 2P_2 - 2\phi_1(P_2 - P_1)}{P_1 + 2P_2 - \phi_1(P_2 - P_1)} \right] $$

(7.9)

where $X_a$ represents the fraction of the composition in which component 1 is the continuous phase and $X_b$ corresponds to a continuous phase of component 2. The description of such co-continuity is limited by the restriction that

$$ X_a + X_b = 1 $$

(7.10)
It can be seen that a composition range in which the permeability data are described by equation with $X_k = X_k$ can be taken as an indication of phase inversion.

Figures 7.9 and 7.10 represent the comparison of experimental results with various theoretical models for NR/ENR-25 and NR/ENR-50, respectively.

**Figure 7.9.** Comparison of experimental results with theoretical models for NR/ENR-25 blends.

**Figure 7.10.** Comparison of experimental results with theoretical models for NR/ENR-50 blends.
The figures show inflection points at volume fractions of 0.3 and 0.7. This probably coincides with the phase inversion. At a volume fraction of 0.5, the permeability of the blend corresponds to the Robesson model. This point corresponds to maximum co-continuity in the system.

7.2 References

9. J. Crank and G. S. Park, (Eds.), Academic Press, New York, 1968, Ch. 1,


