Chapter 5

Interaction of Chlorinated Hydrocarbons with DCP and BP Crosslinked EVA Membranes

Summary

The interaction of dicumyl peroxide and benzoyl peroxide crosslinked EVA membranes with three chlorinated hydrocarbons viz. dichloromethane, chloroform and carbon tetrachloride has been investigated. A significant reduction in diffusion rate and solvent uptake was observed for dicumyl peroxide modified samples. The difference in the sorption behaviour was complemented by the differential scanning calorimetric and scanning electron microscopic analysis. The influence of the nature of penetrants on sorption behaviour was analysed. The effects of different crosslinking agents and varying amounts of crosslinking agents on the tensile properties of the samples were investigated. Sorption, desorption, resorption and redesorption experiments have been performed. The diffusion coefficients of the samples have been estimated together with activation parameters to understand the behaviour of EVA membranes in the presence of different solvents.

Results of this chapter have been published in the journal, Progress in Rubber, Plastics and Recycling Technology, 22, 225 (2006).
5.1. Introduction

The study of the transport of polar and non-polar solvents into polymeric membranes is very important from the practical point of view [1-7]. The low molecular weight haloalkanes released in wasteland fills are known to contaminate ground water, soil and air, causing an immediate threat to human health and hygiene [8]. The use of polymeric membranes for the separation of hazardous halocarbons from organic liquid mixtures, as liners and storage tanks, is increasing. It is important to examine the interaction of different matrices with chlorinated hydrocarbons for the proper selection of the polymer. The changes in the mechanical properties of the membranes after solvent transport, are also important to check their reusability.

Howley et al. [9] examined the factors affecting the diffusion of chlorinated benzene isomers into poly isobutylene and poly (ethylene-co-propylene). The diffusion of chlorinated benzene isomers was employed for the sorption process to determine whether the position of chlorine on the ring affects the diffusion process. It is found that the physical, steric and molecular size effects were found to control the diffusion of these compounds. Duncan et al. [10] investigated the transport properties of methyl chloride and benzene through teflon membranes. In all cases, the permeabilities and diffusivities were independent of the penetrant partial pressure and the permeation process was described by a Henry’s law sorption-Fickian diffusion mode. The diffusional activation energies for
these two substances and other low molecular weight hydrocarbons correlate reasonably well with the Lennarad-Jones collision diameters of the penetrant molecules. The solubilities correlate approximately with the penetrant boiling points, but the highly polar nature of methyl chloride and the aromaticity of benzene lead to deviations in the solubility behaviour. Unnikrishnan and Thomas [11] studied the interaction of crosslinked natural rubber (NR) with chlorinated hydrocarbons. They found that the kinetics of liquid sorption in every case deviates from the regular Fickian trend. The transport properties of irradiated linear low-density polyethylene (LLDPE) were studied by Naddeo et al [12]. The transport properties of a non polar solvent like n-pentane and a polar solvent like dichloromethane, were correlated with changes in the molecular structure and morphology. The formulation of polar groups in the irradiated samples caused a higher sorption of dichloromethane whereas the sorption of n-pentane was found to be dependent only on the amorphous phase.

The goal of the present work is to examine the transport characteristics of DCP and BP crosslinked EVA membranes at ambient temperature, with chlorinated hydrocarbons as probe molecules. A technique is proposed to assess the weight loss during sorption. After sorption, polymer samples were desorbed to measure the amount of sorbed solvent and removal of any residuals. The desorbed samples were again exposed to solvent for resorption followed by redesorption. Thus sorption (S), desorption (D), resorption (RS) and redesorption (RD) tests are effective analytical probes
for studying the molecular transport phenomena. The stress-strain behaviour of the polymers was also studied. Activation energy for diffusion was estimated using Arrhenius relationship.

5.2. Results and Discussion

5.2.1. Processing characteristics

Figures 5.1 (a) and (b) show the rheographs of DCP crosslinked and BP crosslinked EVA membranes respectively. The DCP system has been found to exhibit maximum torque. DCP can cure EVA uniformly and induce more C-C bonds between the macromolecular chain which makes the matrix more rigid. Since maximum torque is a measure of crosslink density and the stiffness of the matrix, it can be concluded that, at the same loading of DCP/BP, more crosslinks were generated by DCP.

![Rheographs of the DCP mixes.](image)

**Figure 5.1(a)**: Rheographs of the DCP mixes.
5.2.2. Differential scanning calorimetric analysis

Differential scanning thermograms of DCP and BP cured EVA samples are depicted in Figure 5.2 (a) and (b). It is seen that T_g and T_m of BP cured EVA samples decreased to -13.2° and 80.3°C respectively. The decrease in the T_g of BP treated sample is associated with increase in amorphous content due to random crosslinking. The lower value of T_m is ascribed to the reduction in crystallinity of BP treated EVA compared to the gum sample. Figure 5.2 (a) revealed that DCP cured EVA has maximum crosslink density and is having higher T_g than BP cured EVA. This is in congruence with the high value of torque obtained in the rheographs (Figure 5.1). High melting point value of DCP cured samples compared to BP treated one is attributed to the increase in crosslink density of the former.
Figure 5.2 (a) : Thermogram of D₁ sample

Figure 5.2 (b) : Thermogram of B₁ sample
5.2.3. Transport analysis

5.2.3.1. Effect of different crosslinking agents

Figure 5.3 shows the effect of different crosslinking agents such as DCP and BP on the solvent uptake behaviour of EVA membranes. The solvent used was chloroform and experiments were conducted at 28°C. BP crosslinked membranes showed a higher equilibrium uptake values. The low uptake of DCP sample is associated with the increase in crosslink density. At the same loading of DCP/BP, DCP produced more crosslinks. The above observation is in accordance with the processing characteristics of DCP and BP crosslinked samples (Figure 5.1 (a) and (b). T_g also supports the above behaviour of crosslinked samples.

![Figure 5.3](image)

**Figure 5.3 :** Effect of different crosslinking agents on solvent uptake.

Figure 5.4 shows the effect of the amount of BP and DCP on the equilibrium mol% uptake of chloroform. The equilibrium mol% uptake of
the crosslinked EVA membranes for all solvents decreases in the order $B_1 > B_2 > B_4 > B_6 > B_8$. It can be seen that BP crosslinked samples showed a higher equilibrium uptake value. This is due to the lower crosslink density values of BP cured samples.

![Figure 5.4: Effect of amount of DCP/BP on equilibrium mol\% uptake.](image)

The $Q_\infty$ values of chlorinated hydrocarbons are found to be higher than that of aromatic and aliphatic hydrocarbons. This is due to the closer solubility parameter values of chlorinated hydrocarbons and EVA samples.

### 5.2.3.2. Morphology

Figures 5.5 (a) and (b) show a comparison between the SEM pictures of $D_1$ and $B_1$ samples respectively. The photographs show that the $D_1$ system is having a more uniform structure. In the $B_1$ sample, the unreacted BP particles agglomerate and hence smoothness of the surface is lost, resulting in a higher solvent uptake.
Figure 5.5: (a) Morphology of D₁ sample

Figure 5.5: (b) Morphology of B₁ sample
5.2.3.3. Effect of nature of penetrants

The influence of the nature of penetrants on the liquid transport through crosslinked EVA samples is presented in Figures 5.6 and 5.7 respectively. Among the three chlorinated hydrocarbons, higher solvent uptake tendency is observed for CHCl₃ when compared to the other two solvents, viz. CCl₄ and CH₂Cl₂. The transport characteristics through a matrix depend upon different parameters, which include the molecular size of the penetrant, its interaction with the matrix and the polarity of the matrix and the penetrant. With crosslinked EVA-aromatic hydrocarbons system, a reduction in equilibrium uptake values was observed with an increase in molecular size of the penetrant (discussed Chapter 3). However, in the case of chlorinated hydrocarbons, the extent of polymer-penetrant interaction has been found to supersede the influence of molecular size. Another important factor which influences the transport is the polarity of the penetrants. The dipole moment of probe molecules are given in Table 5.1. CCl₄ is non polar due to its symmetrical structure but both CHCl₃ and CH₂Cl₂ are polar in nature. Dichloromethane is more polar than chloroform. Since crosslinked EVA samples showed greater affinity towards chloroform, it can be stated that polarity of probe molecules has a little influence on transport. The higher interaction of CHCl₃ with crosslinked system can be explained on the basis of the solubility parameters of the solvent and polymer. The closer the solubility parameters, the greater will be the solubility of the polymer in the solvent. The solubility parameters of the solvents and polymer are given in Table 5.2.
Figure 5.6: Influence of nature of penetrants on transport through D1 sample

Figure 5.7: Influence of nature of penetrants on transport through B1 sample
Table 5.1: Polar characteristics of chlorinated hydrocarbons at 28°C.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Dipole moment (Debyes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>0</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>1.01</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Table 5.2: Solubility parameters (δ) of solvents and polymer

<table>
<thead>
<tr>
<th>Reference</th>
<th>δ (MPa)⁻¹²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>20.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>19</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>18</td>
</tr>
<tr>
<td>EVA</td>
<td>18.8</td>
</tr>
</tbody>
</table>

5.2.3.4. Swelling coefficient (α)

Equilibrium swelling is a measure of swelling resistance of the polymer matrix. In order to assess the extent of the swelling behaviour of the crosslinked samples, D₁ and B₁ samples, swollen in CHCl₃ at room temperature and the swelling coefficients were estimated by the following equation [11]

\[
\alpha = \frac{W_2 - W_1}{W_1 \rho_s} \quad (5.1)
\]
where, $W_1$ and $W_2$ is the weight of the sample before swelling and at equilibrium swelling, respectively and $\rho_s$ is the density of the solvent. Figure 5.8 shows the swelling coefficients of BP and DCP crosslinked samples. The swelling coefficient value of BP crosslinked samples is higher compared to the DCP crosslinked ones. The low swelling values again show that the degree of crosslinking is higher in DCP crosslinked samples.

![Swelling Coefficient](image-url)

**Figure 5.8 :** Swelling coefficients for DCP and BP Samples

Figure 5.9 shows the effect of the nature of penetrants on swelling coefficient values of $D_1$ and $B_1$ samples. Both $B_1$ and $D_1$ samples showed highest value in chloroform. This has been attributed to the strong interaction of chloroform with the polymer matrix, which leads to the swelling of the macromolecular chains.
5.2.3.5. Sorption-desorption-resorption-redesorption (S-D-RS-RD)

The S-D-RS-RD testing of a polymer in the presence of hazardous liquid is important to judge its suitability in field application. Figure 5.10 shows the behaviour of D₁ sample, in chloroform for sorption, desorption, resorption and redesorption.

![Figure 5.9](image1.png)

**Figure 5.9:** Effect of nature of penetrants on swelling coefficient values.

![Figure 5.10](image2.png)

**Figure 5.10:** Sorption, desorption, resorption, redesorption curves of D₁ sample.
The mole percent solvent uptake is higher in resorption than the initial sorption processes. This is due to the leaching out of extra network material, which represents all the unreacted materials left behind in the polymer matrix after vulcanization, during the sorption process [13]. This leads to an increase in free volume in the matrix and hence higher solvent uptake. Initial regions of the sorption and resorption curves are identical in nature and are similar to those of desorption, redesorption curves. The weight change for a sorption-resorption process is 1.72% and that observed for resorption-redesorption is 1.67%. Similar results are shown by BP crosslinked samples also.

5.2.3.6. Mechanical properties of dry and deswollen samples

Table 5.3 shows a comparison of the stress-strain behaviour of dry and deswollen samples in dichloro methane after equilibrium saturation. As expected, the tensile strength is highest for DCP sample. The tensile strength of DCP samples increases from D₁ to D₈. This is due to the increase in crosslink density. For the deswollen samples, no significant reduction in tensile strength has been observed during a sorption-desorption cycle.
Table 5.3: Mechanical properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td></td>
</tr>
<tr>
<td>D₁</td>
<td>6.2</td>
</tr>
<tr>
<td>D₂</td>
<td>7.8</td>
</tr>
<tr>
<td>D₃</td>
<td>8.4</td>
</tr>
<tr>
<td>D₆</td>
<td>9.1</td>
</tr>
<tr>
<td>D₈</td>
<td>9.9</td>
</tr>
<tr>
<td>B₁</td>
<td>5.1</td>
</tr>
<tr>
<td>Deswollen</td>
<td></td>
</tr>
<tr>
<td>D₁</td>
<td>5.8</td>
</tr>
<tr>
<td>B₁</td>
<td>4.6</td>
</tr>
</tbody>
</table>

5.2.3.7. Diffusion coefficient

The diffusion coefficient, D for the different systems, under investigation was estimated using equation 4.3 (Chapter 4). Since significant swelling was observed during sorption experiments, correction of diffusion coefficients under swollen condition was essential. This was done by calculating the intrinsic diffusion coefficient D* using the equation 4.4 (Chapter 4). The values of D* are given in Table 5.4. It can be seen that the D* values are higher for BP crosslinked samples. It is also found that the D* values are highest for chloroform, indicating a higher chloroform-polymer interaction. The above observations complement the solvent uptake nature of the samples.
Table 5.4: Values of intrinsic diffusion coefficient

<table>
<thead>
<tr>
<th>Samples</th>
<th>D* x 10^7 (m^2/s)</th>
<th>Chloroform</th>
<th>Carbon tetrachloride</th>
<th>Dichloro methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁</td>
<td>263.7</td>
<td>39.07</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>D₂</td>
<td>186.3</td>
<td>19.91</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>D₄</td>
<td>22.6</td>
<td>4.22</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>D₆</td>
<td>13.2</td>
<td>2.41</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>D₈</td>
<td>9.15</td>
<td>1.59</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>B₁</td>
<td>304.2</td>
<td>44.6</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>197.4</td>
<td>24.2</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>B₄</td>
<td>32.7</td>
<td>8.1</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>B₆</td>
<td>21.2</td>
<td>5.4</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>B₈</td>
<td>15.4</td>
<td>3.4</td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

5.2.3.8. Activation parameter

To examine the influence of temperature on the transport process, the sorption experiments were conducted at 45 and 55°C in addition to those at 28°C. The sorption curves of D₁ and B₁ in chloroform at different temperatures are given in Figures 5.11 and 5.12, respectively. It has been observed that Q∞ value increases with rise in temperature. The same trend is shown by the B₁ system also. The destruction of long range order in the crystalline regions of EVA coupled with the enhanced macromolecular flexibility at elevated temperature and the increase in
kinetic energy of penetrant molecules accounts for the observed activation of the transport process.

Figure 5.11: Influence of temperature on transport through D₁ sample

Figure 5.12: Influence of temperature on transport through B₁ sample
The diffusion process is temperature activated and hence the energy of activation for diffusion, \( E_D \) is calculated using Arrhenius Equation [14].

\[
D = D_0 e^{-E_D/RT}
\]

(5.2)

where \( D \) is the diffusion coefficient, \( E_D \) is the activation energy for diffusion and \( D_0 \) is a constant. Values of activation energy for diffusion were estimated and given in Table 5.5. The DCP crosslinked sample showed a higher value for \( E_D \). The value of \( E_D \), shows that more activation energy is required for the diffusion through DCP vulcanized samples. The high value shows that more crosslinks are produced in EVA by DCP than BP at the same crosslinker loading. The above observation complements the solvent uptake nature of these samples.

**Table 5.5** : Values of activation parameter

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_D ) KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{CCl}_4 )</td>
</tr>
<tr>
<td>( D_1 )</td>
<td>8.65</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>7.1</td>
</tr>
</tbody>
</table>

5.2.3.9. Crosslink distribution

The solvent sorption behaviour by EVA matrix has been examined in terms of the crosslink distribution in the matrix. Different kinds of networks are formed in a vulcanized polymer system which includes physical and chemical crosslinks. Physical crosslinks consist of chain entanglements
which vary according to the stress developed in the system. The chemical
crosslinks arise from the chemical bonds connecting the polymer
segments. Network macrostructure consists of chain ends, entanglements and crosslink clustering. A schematic model of the macro-structure
network is shown in Figure 5.13. The crosslinks prevent the rearrangement of the chains during the solvent ingression. The complex entanglements and crosslink clusters cause resistance to the path of solvent diffusion.

Figure 5.13 : Schematic representation of macro structural network features (a) Entanglements (b) Chain ends (c) Crosslink cluster (d) Crosslinks

The effect of the degree of crosslinking on the swelling characteristics of the present system can be understood by finding out the crosslink density (ν) by the equation [15].

\[ \nu = \frac{1}{2M_c} \]  
(5.3)
where, \( M_c \) is molar mass between crosslinks. The values of degree of crosslinking suggest that the maximum number of crosslinks per unit volume is possessed by the DCP vulcanized sample and hence it shows the lowest solvent uptake. Figure 5.14 shows the change in crosslink density values with respect to DCP/BP loading. The figure clearly shows that at the same loading of DCP/BP the crosslink density values are higher for DCP.

![Crosslink density vs Amount of crosslinker](image)

**Figure 5.14:** Effect of DCP/BP loading on crosslink density

### 5.3. Conclusion

The transport characteristics of dicumyl peroxide (DCP) and benzoyl peroxide (BP) crosslinked poly (ethylene-co-vinyl acetate) (EVA) membranes, have been studied using dichloromethane, chloroform and carbon tetrachloride as penetrants. Among the three penetrants, both the samples showed the highest solvent uptake values in chloroform. This
has been explained in terms of the solubility parameter values. BP crosslinked samples showed the highest equilibrium uptake ($Q_e$) values than DCP vulcanized samples. At the same loading of crosslinker, dicumyl peroxide produces more crosslinks than BP. This is complemented by the rheographs, glass transition temperature and the values of crosslink density calculated from the sorption data. It has been found that DCP vulcanised samples exhibit good mechanical properties. Also no significant reduction in mechanical properties were observed for the samples after a sorption-desorption cycle.
References


