Chapter 3

Transport of Aromatic Hydrocarbons Through Poly (Ethylene-Co-Vinyl Acetate) Membranes

Summary

The transport behaviour of uncrosslinked and crosslinked poly (ethylene-co-vinyl acetate) (EVA) membranes has been investigated using aromatic hydrocarbons as probe molecules, in the temperature range of 28-70°C. The crosslinker used in the system is dicumyl peroxide. Diffusion through membranes containing different loading of DCP was also carried out. The observed reduction in the solvent uptake of uncrosslinked EVA is due to the presence of crystalline regions in the matrix. It has been found that, as the extent of crosslinking increases the equilibrium uptake decreases. The mechanism of transport has been found to deviate from the regular Fickian behaviour. The effect of penetrant size on the sorption behaviour of EVA was investigated. The processing characteristics and the morphology of the membranes were also discussed for complementing the results of sorption studies. Finally, the experimental sorption data were compared with theoretical predictions.

The results of this chapter have been published in Polymer 38, 4629, 1997 and an extension of this work has been published in the Journal of Material Science, 41, 4892, (2006).
3.1 Introduction

The wide range applications of polymers as barrier materials have created a great interest in the transport of organic liquids through polymers [1, 2]. The results on the behaviour of aromatic solvents with polymers are very much important in technology because of the sensitivity of the polymers to these solvents. The swelling of polymeric materials in aromatic solvent environment is highly essential for the areas such as controlled release systems [3] and hazardous waste water treatments [4]. Aromatic hydrocarbon – polymer interaction has been extensively studied and reviewed by many researchers [4-8]. Markevich et al. [9] investigated the sorption and diffusion of toluene through blends of low density polyethylene (LDPE) and poly (vinyl chloride) (PVC). LDPE is active and PVC is inactive towards toluene. Schneider et al. [10] examined the concentration dependence of the diffusion coefficient of toluene in butyl rubber over a wide range of concentrations. The influence of polymer structure and penetrant molecular size on the sorption and diffusion of substituted benzenes through commercial polymeric systems was investigated by Aminabhavi and coworkers [11,12]. Walksman et al. [13] investigated the diffusion of toluene through natural rubber (NR). The sorption rate curves, which were no longer Fickian above a moderate concentration, showed a slight ‘S’ shaped curvature suggesting that relaxation effects might be involved in the swelling behaviour. This relaxation may arise from the slow response of the network structure to the
swelling stresses. Kumar and Siddaramaiah [14] studied the sorption and desorption of aromatic probe molecules into semi-interpenetrating network of polyurethane/polymethyl methacrylate. Sorption and diffusion results measured at different temperatures viz. 20, 40 and 60°C are found to follow Fickian mechanism. The mass uptake values decreased with increase in crosslink density. The rate of evaporation of liquids has been calculated for desorption and redesorption runs and these results depend on volatility of solvents. Chao et al. [15] investigated the permeation of aromatic hydrocarbons through high density polyethylene geo membranes. They found that the diffusion coefficients and solubilities of organic solvents correlated well with their molecular weights and dipole moment. Our group also conducted the examination of the interaction of aromatic solvents with different polymeric systems [16,17].

This chapter deals with the investigation on the transport behaviour of three aromatic hydrocarbons viz. benzene, toluene and xylene through uncrosslinked and DCP crosslinked EVA membranes in the temperature range of 28-70°C with special reference to the effects of crystallinity, introduction of crosslinks, penetrant size and temperature.

3.2. Results and Discussion

3.2.1. Processing characteristics

The cure characteristics of the samples have been studied from the rheographs. Figure 3.1 shows the rheographs of DCP crosslinked EVA samples. The initial decrease in torque is due to the softening of the
matrix. Torque then increases due to the formation of C-C crosslinks between the macro-molecular chains. The leveling off is an indication of the completion of the curing process. The maximum torque in the rheograph is a measure of crosslink density and the stiffness of the matrix.

Figure 3.1: Rheograph of the mixes

### 3.2.2. Transport analysis

#### 3.2.2.1. Effect of crystallinity

Figure 3.2 shows the sorption curves of uncrosslinked EVA (D₀) and DCP crosslinked EVA (D₁) at 28°C. The solvent used was benzene. The uncrosslinked EVA shows a lower solvent uptake (Qᵣ, mol%) than D₁. Similar trends were also observed with toluene and xylene.
Figure 3.2: Mol\% benzene uptake of uncrosslinked and crosslinked sample at 28°C

The low solvent uptake for the uncrosslinked EVA is due to the presence of crystalline regions in the matrix. The long range order generates a compact structure and hence a lower porosity. The porosity is increased by the presence of moderate amounts of DCP due to the formation of C-C bonds between EVA chains. This is illustrated schematically in Figure 3.3. The X-ray diffraction patterns (XRD) of the uncrosslinked and crosslinked EVA support the above data and are given in (Figure 3.4). It has been found that crystallinity is substantially reduced in the crosslinked sample.
Figure 3.3: Schematic representation of the morphology of (a) uncrosslinked and (b) crosslinked EVA

Figure 3.4: X-ray diffraction patterns of uncrosslinked and crosslinked membranes
The above results have been correlated with the morphology of the matrix, examined with transmission electron microscopy (TEM) given in Figure 3.5. The crystalline nature of EVA is evident from the photograph and on addition of DCP, the volume of amorphous phase increases.

![Figure 3.5: TEM photographs](image)

**Figure 3.5**: TEM photographs

### 3.2.2.2. Effect of crosslinker loading

Figure 3.6 shows the sorption curves of EVA samples crosslinked with different amounts of DCP. The equilibrium mol% uptake of the crosslinked EVA samples for all solvents decrease in the order $D_1 > D_2 > D_4 > D_6 > D_8$. When the amount of DCP is increased, the extent of crosslinking goes up and this prevents the migration of the solvent molecules into the network. As the crosslink density increases, the contribution of the crosslink constraints, on the penetrant chemical potential becomes stronger and
solvent uptake decreases accordingly. In fact, the decrease in crystallinity is offset by the increase in crosslinking density.

![Graph showing mol% benzene uptake of crosslinked samples at 28°C](image)

**Figure 3.6**: Mol% benzene uptake of crosslinked samples at 28°C

### 3.2.2.3. Effect of penetrant size

The sorption curves of D₁ sample in three different aromatic hydrocarbons are presented in Figure 3.7. There is a systematic trend on the sorption behaviour of liquids with different molecular size. With an increasing size of solvent molecule there is a decrease in the solvent uptake. It has been observed that among the solvents used, benzene uptake is maximum while xylene uptake is minimum and toluene takes an intermediate position. The decrease in mol% uptake with increase in penetrant size is due to the greater activation energy required for activating the sorption
The effect of molecular mass of the solvent on the equilibrium mol% uptake, $Q_\infty$, is illustrated in Figure 3.8.

**Figure 3.7**: Mol% solvent uptake of D₁ sample at 28°C

**Figure 3.8**: Effect of molar mass of the penetrants on equilibrium uptake
3.2.2.4. Mechanism of sorption

The mechanism of the penetrant transport into a polymer has been analysed in terms of the empirical relation [18].

\[
\log \frac{Q_t}{Q_\infty} = \log k + n \log t 
\]  

(3.1)

where \(Q_t\) is the mol\% solvent uptake at a time \(t\) and \(Q_\infty\) is the equilibrium mol\% solvent uptake. The factor, \(k\), is a constant and it depends on the structural characteristics of the polymer and also on the polymer – solvent interaction. The value of ‘\(n\)’ determines the mode of sorption mechanism. For the Fickian mode, the value of \(n\) is 0.5 and it occurs when the rates of diffusion of the permeant molecules are much less than the relaxation rates of the polymer chains. If the value of \(n\) is 1, the mode of diffusion is non-Fickian and it arises when the rates of diffusion of permeant molecules are much faster than the polymer relaxation process. When the value of ‘\(n\)’ lies between 0.5 and 1, the mode of diffusion is anomalous. This occurs when the rates of permeant mobility and polymer relaxation process are similar. Plots of log \((Q_t/Q_\infty)\) vs. log \(t\) were constructed and the data up to 50% sorption from the sorption curves were used to compute the values of \(n\) and \(k\). A linear regression analysis was used to get the values of \(n\) and \(k\), and the estimated values are compiled in Table 3.1. For samples at 28°C, the value of ‘\(n\)’ ranges between 0.52 and 0.65, indicating an anomalous mode of diffusion. For all samples, the values of \(k\) are found to decrease gradually with an increase in the molecular size of the aromatic hydrocarbons suggesting a decreased polymer-solvent interaction.
Table 3.1: Analysis of sorption data of aromatic hydrocarbons in EVA at 28°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>n</th>
<th>K x 10⁻² (g/g min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D₀</td>
<td>D₁</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.56</td>
<td>0.59</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.53</td>
<td>0.60</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.52</td>
<td>0.57</td>
</tr>
</tbody>
</table>

3.2.2.5. Effect of temperature

The temperature dependence of diffusion through the crosslinked EVA systems was followed by conducting the experiments at 50 °C and 70°C in addition to 28°C. In Figure 3.9, Q₁ mol% uptake is plotted as a function of time at various temperatures for the D₁ system. The solvent used is benzene. It has been observed that Qₘ values increase with increasing temperature. The same trend is also shown by other systems in all solvents. The increase in solvent uptake is due to the increase in free volume and greater segmental mobility at higher temperatures. With the uncrosslinked systems, the high temperature diffusion experiments were not possible because the samples were found to be dissolved by the solvent at higher temperatures.
Figure 3.9: Temperature dependence of mol\% uptake of D\textsubscript{1} sample

It has also been observed that the slope of the linear portion increases with temperature indicating that the transport process is temperature activated.

3.2.2.6. Sorption kinetics

Earlier it was shown that transport of liquids through polymer membranes is considered as a rate controlled kinetic process which can be followed by the first order kinetics \[19\]. During diffusion and sorption of liquids through polymer membranes a structural rearrangement occurs in the polymer matrix and this will induce kinetic behaviour. Kinetics mainly depends on the segmental mobility and availability of free volume within the matrix. The first order equation is given below:

\[
d_{t}/d_{t_{0}} = k_{1} (C_{\infty} - C_{t})
\]  
(3.2)
which on integration gives

\[ k_1 t = 2.303 \log \left( \frac{C_\infty}{C_t} - C_t \right) \]  

(3.3)

where \( k_1 \) is the first order rate constant (min\(^{-1}\)). \( C_t \) and \( C_\infty \) represent concentration at time \( t \) and at equilibrium. Plots of \( \log (C_\infty - C_t) \) vs. time is shown in Figure 3.10. The kinetic rate constant is a measure of the speed with which the solvent molecules migrate within the polymer matrix. It is found that all the plots are linear showing that diffusion follows first order kinetics.

\[ \frac{d\omega}{dt} = k_2 (C_\infty - C_t)^2 \]  

(3.4)
where $k_2$ is the second order rate constant. The integrated form of the equation is

$$k_2 t = 1/ C_\infty - C_t - 1/ C_\infty$$  \hspace{1cm} (3.5)

The typical second order kinetics plot of aromatic hydrocarbons at $28^\circ$C for the D$_1$ system is given in Figure 3.11. The plot is slightly curved in the middle. Since a straight line graph is obtained for first order kinetics, it seems to be more appropriate than second order kinetics for the transport of aromatic hydrocarbons through EVA.

![Second order plots for the D$_1$ sample at 28°C](image)

**Figure 3.11**: Second order plots for the D$_1$ sample at $28^\circ$C

### 3.2.2.7. Comparison with theory

The experimental diffusion coefficients were compared with theoretical predictions. The theoretical sorption curves were generated using the equation [21].
where \( Q_t \) and \( Q_\infty \) are the mass of solvent uptake at time \( t \) and at equilibrium, \( D \) is the diffusion coefficient and \( h \) is the thickness of the polymer sample. This equation describes a Fickian mode of diffusion. Experimentally obtained values of diffusion coefficients are substituted in the above equation and the resulting curves obtained are shown in Figures 3.12 & 3.13.

Figure 3.12 gives a comparison of the experimental and theoretical diffusion curves of \( D_1 \) sample at 28°C in toluene. Theoretical and experimental results were not in good agreement. The experimental curve deviates from the theoretical curve which is fully a Fickian mode of diffusion. The deviation is also evident from the value of \( n \). Figure 3.13
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gives the comparison of experimental and theoretical curves of $D_8$ sample at $28^\circ C$. Here also the same trend is observed.

3.3. Conclusion

The transport of aromatic hydrocarbons through EVA has been studied by the use of sorption gravimetric analysis. The result of these studies on polymer-solvent interaction are important in the successful application of these materials in pervaporation experiments and barrier packagings. It has been found that the introduction of crosslinks in EVA has profound influence on the transport process. The solvent uptake tendency of uncrosslinked sample was found to be low due to the crystalline nature of the polymer. For the crosslinked samples, solvent uptake tendency decreased in the order $D_1 > D_2 > D_4 > D_6$. This is mainly due to the increase in the extent of crosslinking. As the penetrant size increased the maximum solvent uptake decreased. The mechanism of diffusion deviates from the normal Fickian behaviour. At higher temperatures, equilibrium penetrant uptake was high due to the increase in the polymer free volume. Transport kinetics has been studied in terms of the first and second order kinetics. However, first order kinetics seem to be more appropriate for the systems studied. The experimental diffusion results were found to deviate from the theoretical predictions.
References


