Chapter 7

Transport of Chlorinated Hydrocarbon Vapours
Through Poly (ethylene-co-vinyl acetate) Membranes

Summary

The permeation of chlorinated hydrocarbon vapours through uncrosslinked and crosslinked EVA membranes has been analysed. Uncrosslinked samples showed the least permeation coefficient value. The effects of crosslinker loading and penetrant size on vapour permeation have been analysed.

The results of this chapter have been communicated for publication in Polymer Bulletin
7.1. Introduction

Vapour permeation process is defined as the transport of a condensable vapour through a dense membrane. This process offers the unique feature of studying the transport process of a single permeant through a dense membrane under various upstream activities [1-3]. Such characteristics can no means be obtained by liquid permeation, where the modification of the upstream activity of a component can only be achieved by adding another compound to the mixture; the activity of both components is modified in this case in compliance with Gibbs-Duhem equation, which complicates the transport analysis. On the contrary, coupling phenomena are not to be considered with pure vapour permeation results. In the case of pure permeation, upstream activity can be easily calculated, provided upstream pressure is precisely monitored [4].

Besides these advantages, a study of solvent vapour permeation offers direct practical conclusions for the understanding and rational design of volatile organic components (VOC) vapour recovery from contaminated air stream [5]. Vapour permeation also offers significant opportunities of energy saving and solvent reuse, compared to classical VOC control processes such as incineration, oxidation or active carbon adsorption.

Vapour permeation is based on the vapour permeability and partial pressure difference between the feed side and permeate side stream [6]. A method was developed for simultaneous determination of the permeability, diffusion and solubility coefficients of organic vapours.
through polymers from the mass transfer through polymer membranes. The sorption and diffusion coefficients of acetylene, ethylene, ethane, propane, butane, pentane and xenon in poly (trimethyl vinyl silane) were determined by sorption-desorption method [7]. Sansone and Tewari [8] calculated the permeability coefficient of vapours of benzene in air from the measured values of solubility and diffusity. Yampolskii et al. [9] reported the thermodynamics of gas and vapour sorption by amorphous glassy teflons. They found that vapour solubility coefficient increases with the content of perfluorodioxal monomers. Fornasiero et al. [10] reported the vapour sorption characteristics of 4-vinylpyridine based copolymer.

In this chapter, the influence of the sorption and diffusion processes in the overall permeation rate of organic vapours through EVA membranes were examined. Besides this, the influence of crystallinity, crosslinker loading, and various crosslinking agents on the vapour permeation of chloro hydrocarbons through EVA membranes have also been examined.

7.2. Results and Discussion

7.2.1. Theory

The permeation of organic vapours through polymeric membranes is usually believed to follow a solution-diffusion process [11-13]. Thus permeability (P) is the product of solubility coefficient (S) and diffusion coefficient (D).

\[ P = D \times S \]  (7.1)
The factors affecting the permeability of a polymeric film are nature of the polymer, solubility, molecular weight and shape of the penetrant [14-16].

7.2.2. Influence of crystallinity and crosslinking on vapour permeation

Table 7.1 shows the permeability coefficients of uncrosslinked (D₀), BP and DCP crosslinked EVA membranes. The solvent used was chloroform. It can be seen from the table that the uncrosslinked membranes showed the least value of permeability coefficient. In the case of unmodified EVA, which is a semi crystalline polymer, the compact crystalline regions do not allow the permeation of vapours through it. The presence of crystalline regions generates a more tortuous path for the penetrants and subsequently, the rate of vapour ingression and the permeability decreases.

<table>
<thead>
<tr>
<th>System</th>
<th>Permeability</th>
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<tbody>
<tr>
<td>EVA</td>
<td>7.2</td>
</tr>
<tr>
<td>D₁</td>
<td>7.6</td>
</tr>
<tr>
<td>B₁</td>
<td>8.02</td>
</tr>
</tbody>
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The crosslinked samples (D₁ and B₁) showed highest vapour permeation due to the increase in amorphous phase of the matrix. When EVA was crosslinked by DCP or BP, the crystallinity was reduced due to the formation of C-C networks. The above situation is schematically represented in Figure 7.1.
Among the crosslinked samples, BP modified EVA membranes showed highest vapour permeability. This is due to the fact that at the same loading of BP/DCP, maximum crosslinks were generated by DCP molecules. When the number of crosslinks increase, the available free volume and the flexibility of the matrix decreases. This results in the reduced permeability of DCP modified membranes.

7.2.3. Influence of crosslinker loading on vapour permeation

Figure 7.2 shows the effect of crosslinker loading on the vapour permeability of EVA membranes. It can be seen that as the amount of the crosslinker increases, the vapour permeability decreases. When the amount of DCP increases, the polymer matrix contains large number of rigid C-C linkages which do not allow the chain to rearrange under the organic vapour stress. This accounts for the lowest vapour permeability of $D_8$ system.
7.2.4. Influence of penetrant size on vapour permeation

Figure 7.3 shows the influence of nature of the penetrants on the vapour transport through DCP crosslinked EVA membranes. Among the three chlorinated hydrocarbons, higher vapour permeability is observed for chloroform compared to other solvents, viz. CCl₄ and CH₂Cl₂. The transport of vapour depends upon various factors, which include the molecular size of the penetrant and its interaction with the matrix. In the case of chlorinated hydrocarbons, the extent of matrix-penetrant interaction has been found to supersede the influence of molecular size. The above results are similar to the liquid transport characteristics of EVA discussed in chapter 5. The above observation can be explained on the basis of the solubility parameter values. EVA and CHCl₃ have closer solubility parameter values compared to other systems.
Figure 7.3 : Influence of size of the penetrants on permeability

7.3. Conclusion

Transport of chlorinated hydrocarbon vapours through EVA membranes have shown that the permeation behaviour vary according to the structure of the material. Uncrosslinked EVA membranes showed least permeability. When crosslinked by DCP or BP, the vapour permeability was increased due to the reduction in the crystallinity of the matrix. EVA membranes crosslinked by BP showed maximum vapour permeability. It is also observed that crosslinker loading has a significant influence on permeation behaviour. Among the penetrants chloroform showed maximum vapour permeability.
References


