Chapter 9

Vapour Permeation Properties of EVA/Clay Nanocomposites

Abstract:

The vapour transport through the nanocomposite membranes was investigated and the results were compared in this chapter. Studies revealed that the incorporation of nanoclay in the polymer increased the efficiency of the membranes towards barrier properties. Due to the aggregation of nanoclay at higher loadings, it was found that the permeability of the vapour increased. Better barrier properties were obtained for Cloisite25A based nanocomposites compared with other samples. The dispersion of clay platelets seemed to be maximized for 3 wt% of clay and agglomeration increased with higher clay loading. Finally, the experimental permeability results have been correlated with Bhardwaj model. Data gave reasonably good fitting.
9.1. Introduction

The barrier properties in polymers can be broadly defined as macromolecules having the ability to significantly restrict the passage of gases, vapours, and liquids. Poly(ethylene-co-vinyl acetate) had a special attention to restrict the transport of penetrants to some degree and the barrier performance depends on a variety of factors. In a practical sense, however, the definition of a barrier polymer depends upon the end user requirements, and a material that provides sufficient barrier for a particular application can be considered to be a barrier polymer for that purpose. The permeation of plastic films and other packaging materials to gases and vapours is of practical interest. The permeability constants of water vapour, CO₂ and oxygen are needed for the design of packing materials. The food packaging industry places particular demands on the barrier properties of their products. While many barrier membranes are designed to prevent the permeation of hydrophilic substances, such as water, other barrier membranes are designed to reduce permeability to hydrophobic substances, such as many toxic chemicals.¹ On the other hand, in order to reduce the cost while still maintaining good processibility and barrier properties of the barrier resins, compounding of a polymer with nanoscale filler particles with high aspect ratio has drawn much attention recently.²,³ It was reported that the permeability through the polymer films can be reduced with small loadings of nanoclay.⁴ The impermeable clay layers force a tortuous pathway for a permeate transverse the nanocomposites.

Tang et al.⁵ melt blended EVA with organophilic MMTs such as hexa-decyl and octa-decyl ammonium ions at about 145 °C to obtain EVA/clay nanocomposites. In these EVA/clay composites, individual silicate layers were exfoliated in the polymer matrix in a nanometer range along with some
large, intercalated tactoids. Marini et al.\textsuperscript{6} reported that nanoclays modified with polar groups make an exfoliated structure with polar polymers more efficiently. Many authors have studied poly(ethylene-co-acetate) matrices formed of clays with distinct segments and alkyl chain lengths.\textsuperscript{7–9} Khounlavong and Ganesan\textsuperscript{10} observed that the addition of impenetrable nanofillers into a rigid polymer matrix resulted in the enhancement of the composite membrane’s permeability to gas penetrants and they noted the influence of interfacial layers on transport properties. Martínez-Sanz et al.\textsuperscript{11} studied the water barrier properties of ethylene vinyl alcohol copolymer (EVOH) nanocomposites prepared by melt compounding and incorporating both plant and bacterial cellulose nanowhiskers. An improvement in the water barrier performance was observed by incorporating 2 wt\% of bacterial cellulose fibrils in the sample.

Seethamraju et al.\textsuperscript{12} studied the efficiency of moisture barrier films based poly (vinyl alcohol-co-ethylene) with surface modified montmorillonite. It was noted that the transmission rate of water vapour through the composite films, which showed a gradual reduction with increasing modified montmorillonite loading in the neat copolymer. The increase in moisture barrier performance is attributed to the decreased water vapour diffusivity due to matrix–filler interactions in the composite. Mondal et al.\textsuperscript{13} reported in the hydroxylpropylmethylcellulose (HPMC)/montmorillonite (MMT) nanocomposite films by solution intercalation method, the moisture absorption of these films in 75\% of constant relative humidity is reduced with loading of MMT. The water vapour transmission rates (WVTR) through a series of poly(lactic acid) (PLA) nanocomposites containing from 1 up to 6 wt\% of montmorillonite layered silicate films studied by Duan et al.\textsuperscript{14} From their study it was found that the measured values of WVTR decreased with increasing nanoclay
content up to a value of 5 wt% and the results gave good agreement with theoretical predictions. Polylactide–montmorillonite composites were fabricated by Du et al.\textsuperscript{15} The water permeability of composites decreases with increasing concentration of montmorillonite. It was also noted that at a concentration of 10 wt% of montmorillonite, the water permeation is 34% less than in the neat polymer. A lot of reports were in literature for the vapour sorption characteristics in polymer nanocomposites.\textsuperscript{16-24}

In this chapter, nanocomposites with poly(ethylene-co-vinyl acetate) (EVA) and four different organically modified clay with varying clay loadings (3, 5, 7 wt %) were prepared. The vapour transport properties of chlorinated hydrocarbons through the nanocomposites were analyzed in detail and the experimental values were fitted with Bharadwaj model.

**9.2. EVA/clay nanocomposite membrane for vapour permeation**

**9.2.1. Permeation co-efficient**

The permeation coefficient ‘P’ of the EVA/clay nanocomposites, for the permeation of CCl\textsubscript{4}, CHCl\textsubscript{3} and CH\textsubscript{2}Cl\textsubscript{2} has been calculated using the equation 9.1

\[
P = \frac{QL}{pAt} \quad \text{..................(9.1)}
\]

‘L’ is the membrane thickness, ‘Q’ is the molar quantity of solvent permeating through the membrane area ‘A’ during a certain time ‘t’ under a steady state condition. ‘p’ is the difference in vapour pressure of the solvent, across the membrane.
Vapour permeation properties of EVA/clay nanocomposites

Figure 9.1: The graphs of chloroform permeation through the EVA/clay nanocomposites

The permeation was analyzed for the four series of nanocomposites, for example B series of nanocomposites were shown in Figure 9.1. It was found the permeability of chloroform was decreased by the incorporation of the nanoclay in the polymer matrix. The lowest permeation was found in for 3 wt% clay loading; this may be due to the nice dispersion of the nanoclay in the polymer matrix at the lower loading. At higher concentration of clay contents, the permeation was found to be increasing. This is mainly due to the agglomeration of clay platelets at higher clay loadings as discussed
earlier by TEM results. Agglomeration results in increased free volume and hence the permeability increases. Similar type of behaviour was shown by the other nanocomposites (A, C and D). This was in complement with the TEM images and PALS analysis. The nano particles lead to the presence of internal interfaces within the material that may play a role in the permeation process. Strong affinities between surfaces and diffusing molecules may provide a driving potential for diffusion in addition to concentration gradients (or supply regions where the local concentration of diffusing molecules far exceeds the solubility limit of the matrix). Strong interactions between surfaces and diffusing molecules may allow for increased rates of diffusion along the interfaces. Conversely, strong interactions between diffusing molecules and particle surfaces may reduce permeation rates. Strongly absorbed molecules will need to overcome an energy barrier to desorbs, and thus are likely to be far less mobile than molecules dissolved in the polymer matrix. This mechanism, combined with the increased diffusion path lengths due to the particles, is supported by observation that the addition of nano-fillers (such as clays) can significantly reduce permeability.\textsuperscript{25}

![Permeation graphs](image)

**Figure 9.2:** The graphs of (a) dichloromethane and (b) carbon tetrachloride through the different type of clay system
From the Figures 9.2 (a and b), it can be noted that lowest permeation was shown by D_3 series of nanocomposites. This may be due to the better interaction of D series of nano-clay with the polymer matrix. It was evident from the TEM and X-ray analysis.

9.2.2. Polymer–Solvent interaction parameter

Polymer-solvent interaction parameter was determined using the equation

\[
\chi = \beta + \frac{\nu}{V} (\delta_s - \delta_p)^2
\]

where, \(\delta_s\) and \(\delta_p\) are the solubility parameters of the solvent and the polymer, \(\beta\) the lattice constant, \(R\) is the universal gas constant and \(T\) is the absolute temperature. The polymer–solvent interaction parameter is a dimensionless parameter, which characterizes the interaction between one polymer segments with the solvent molecule. Several studies have been reported on the role of the interaction parameter on diffusion.\(^{27,28}\)

**Table 9.1: Values of interaction parameter (\(\chi\)) for EVA system**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>EVA Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>0.81</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0.78</td>
</tr>
<tr>
<td>CCl₄</td>
<td>1.87</td>
</tr>
</tbody>
</table>

A low value of interaction parameter indicates a stronger interaction with the solvents. The calculated values are placed in Table 9.1. The values of \(\chi\) for
EVA polymer in the three solvents decreases in the order carbon tetrachloride > dichromomethane > chloroform. Hence polymer/solvent interaction is high for chloroform and lowest for carbon tetrachloride.

The kinetic gravimetric sorption experiments are widely used for such large and condensable penetrants at low thermodynamic activities (i.e., low relative pressures). For this reason, data are often reported for such species based on experiments performed by exposing samples to saturated vapours or immersing them in liquid penetrant and weighing the samples at regular time intervals, effectively yielding sorption and transport measurements at very high activity. Since penetrant solubility and diffusivity are often strongly dependent on concentration (or activity).
Figure 9.3: The permeation graphs of different solvents through EVA / clay nanocomposites

The permeation process has been found to be controlled mainly by the interaction parameter of the penetrants, in an expected way. CHCl₃ vapours permeated more rapidly through the membrane, due to lower value of interaction parameter, the solvent molecules, which can more easily pass through the free volumes of the membrane than the CH₂Cl₂ molecules or the CCl₄ molecules. Thus the order of vapour permeation has been found to be according to the penetrant size i.e., chloroform > dichloromethane > carbon tetrachloride. Wang et al.³¹ noted that the plasticizing effects of permeates and the interaction between permeates and polymer play a significant role in the permeation process.

The vapour permeation can be highly dependent on interaction between the diffusing species and the polymer. The concentration of diffusing molecules within the polymer may influence their diffusion properties. Diffusion is driven by concentration gradients and so, initially, high external concentrations imply high concentration at the surface causing large concentration gradients and, hence, rapid diffusion. As time progresses, the system will reach an equilibrium concentration determined by the solubility and external concentration. For example, if the polymer swells in response to absorption of the diffusing molecules then increasing concentrations may increase the diffusion mobility by causing additional free volume as the polymer swells further. In the absence of such interactions, increasing concentrations in the material may lead to ‘crowding’ of absorption sites and reducing diffusion. Anusree et al.³² noted the vapour permeation characteristics in natural rubber/poly(ethylene-co-vinyl acetate) (NR/EVA) blend membranes, cross linked with dicumyl peroxide. The permeability was
found to decrease with increase in EVA content which has been attributed to
the semi crystalline nature of EVA. The vapour permeation process has been
observed to be controlled by the interaction of acetone with blend system in
the case of benzene/acetone mixtures. Kutty et al.\textsuperscript{33} conducted the vapour
permeation studies on ethylene propylene diene monomer (EPDM) and
polyvinyl chloride (PVC) with aromatic hydrocarbons and aliphatic alcohols.
The permeability was found to decrease with increase in PVC content due to
the stiff and rigid nature of PVC. Different types of miscible liquid mixtures
have been analyzed for finding out the separation efficiency of the
membranes. In the case of benzene/propanol mixture, it has been found that
when the concentration of benzene increases, the vapour permeation rate
increases, indicating high interaction of benzene toward the composites.

\textbf{9.3. Permeation models}

Because of the barrier role of silicate platelets, a diffusing liquid molecule
must travel more distance in between the sheets forming a very tortuous
path. Therefore, the factors influencing the permeability of polymer layered
silicate nanocomposites are mainly dependent on the degree of exfoliation or
intercalation and the state of dispersion of silicate platelets in polymeric
matrix, such as aspect ratio L/W (L and W, are length and thickness of
silicate platelets, respectively), orientation, dispersion spacing between two
sheets, volume fraction etc. Nielsen model has been applied to predict the
dependence of gas permeability on the filler volume fraction.\textsuperscript{34} This model
introduced the basic concept of tortuosity factor to predict the effective
permeability as a function of volume fraction of clay

\[
\frac{P}{P_0} = \frac{1 - \phi}{1 + (\phi/2)\phi}
\]

\textbf{........................(9.3)}
Where $P$ and $P_0$ are the permeabilities of the composite and that of neat polymer respectively, $\phi$ is the volume fraction of the filler and $\phi$ is the aspect ratio. In Nielson model, the dependence of permeability on the relative orientation and state of dispersion of the clay platelets is not taken into consideration.

The tortuosity factor is modified by including the orientational order by Bharadwaj model and the relative permeability is given by\(^{35}\)

$$\frac{P}{P_p} = \frac{1-\phi_\phi^2}{1+\frac{2}{\phi_\phi^2}(\phi_\phi^2-1)}$$

Equation (9.4)

Where $P_s$ is the permeability of the EVA/clay nanocomposites, $P_p$ is the permeability of the pure EVA, $L/W$ ($\phi$) is the aspect ratio. The key parameters of this model are the dispersed phase volume fraction of impermeable fillers $\phi$, the particle aspect ratio $\phi$, and the orientation parameter of the clay platelets, $S$, which was chosen equal to 0, corresponding to particle random distribution ($S= 1/2(3\cos^2 \theta -1)$, $\theta$ angle between direction of preferred orientation and the sheets normal. When $S=1$ (planar arrangement) and converges approximately to the permeability of the pure polymer when $S=-1/2$ (orthogonal arrangement). The barrier property is enhanced when $S=1$ and decays in a continuous fashion as predicted in the equation nearly that of the pure polymer when $S=-1/2$ where the sheets are supposed to be arranged such that there is negligible decrease in the tortuosity. The various orientations of the silicate layers are schematically represented in the Figure 9.4.
Figure 9.4: The three different type’s orientation of silicate layers in polymer matrix

Figure 9.5: Experimental data fitted with Bharadwaj model for CH$_2$Cl$_2$ solvent

Experimental data of permeation were fitted in equation 9.4. Considering random particle orientation (S=0), the calculated aspect ratio was found to be 199 for A series of samples, 210 for B series, 205 for C series and 235 for D series of nanocomposites. Manninen et al.$^{36}$ indicated that the processing
path taken to prepare the nanocomposites may result in agglomeration of the organoclay layers. These agglomerates may cause the formation of large scale holes (pores) in the matrix, which can act as low resistance pathways for gas transport within the nanocomposite. In such a case the diffusion becomes mostly of the Knudsen flux type. For high clay contents, it is difficult to keep a high degree of platelet dispersion and avoid the presence of intercalated structures. In chlorobutyl/montmorillonite nanocomposites, e.g., the obtained aspect ratio decreased with increasing $\phi$, using either modified or non-modified particles.\textsuperscript{37} The experimental permeability values of A samples were fitted into the Bharadwaj model and Figure 9.5 shows the experimental and theoretical curves. The results are in line with the prediction by Bharadwaj model. However, at higher concentration of clay, experimental curve deviates from theoretical curve. This is mainly due to the agglomeration of clay platelets at higher clay loadings.

9.4. Conclusions

From this study it can be clearly understood that that the barrier properties of EVA are improved by the incorporation of nanoclay in the polymer. The permeability was found to be lower for the $\text{CCl}_4$ and maximum for the $\text{CHCl}_3$ due to difference in the interaction parameters between solvent and polymer. The permeability of the nanocomposites was very much reduced at lower filler loading of nanoclay and the permeability was increased at higher loading due to the filler agglomeration at higher loading. Experimental permeability values have been compared with the permeability values obtained using Bharadwaj’s permeability model. There is good agreement at the low filler loadings. The level of agreement suggests that the fillers have a random distribution in the matrix.
9.5. References


26. Hildebrand J. H.; Scott R.L. *The Solubility of Non-Electrolytes*, (Reinhold: New York, **1949**).


