Chapter 7
Permeability Through Nanocomposite Membranes

Abstract

This chapter describes the gas permeability of nanocomposites with fillers of different size and shape. The gas transport behaviour has been investigated with special reference to filler geometry and filler loading. The layered silicate filled system showed outstanding enhancement in gas barrier property in comparison with nano Ca$_3$(PO$_4$)$_2$ and more spherical TiO$_2$. The variations in barrier properties could be attributed to the extent of intercalation/exfoliation which was highly influenced by the filler geometry of the layered silicate.

*Part of the results of this chapter have been communicated to Journal of Membrane Science*
7.1 Introduction

Polymer-layered silicate nanocomposite are believed to have much increased physical properties in comparison with the virgin polymer [1-6]. Nanoscopic dispersion of the layered silicate in a polymer matrix results in a greater enhancement in gas barrier property compared to conventional phase separated composites by creating a maze or ‘tortuous path’ that retards the progress of the gas molecules through the matrix resin [7-10]. The transport of gases through polymeric membranes depends on the size, shape and phase of permeant, molecular weight, structure, crystallinity, crosslinking etc of the polymer [11]. The relationship between gas transport and the structure of the matrix has been studied by Paul and co-workers [12,13]. Gas transport through nano and micro composites of natural rubber (NR) and their blends with carboxylated styrene butadiene rubber (XSBR) latex membranes was studied by Stephan et al. [14] with special reference to type of filler, gases, filler loading and pressure. They observed that due to the platelet like morphology and high aspect ratio of layered silicates, the gas barrier properties of nano filled latex membranes were very high. Johnson and Thomas [15] analyzed the gas transport properties of different rubber blends and arrived at a conclusion that permeation is a process in which gas molecules dissolve in the elastomer on one side of a membrane, diffuse through it to the other side and then evaporate. Recently, Varghese et al. [16, 17] studied the properties of natural rubber and synthetic rubber lattices reinforced with layered silicates. The introduction of functional groups in the polymer chain can alter the permeability and selectivity due to the variation in the existing free volume within the polymer [18, 19].
The selective transport of gases through polymeric membranes has been reviewed by Aminabhavi and co-workers [20]. Water-vapour permeability of NBR/MMT nanocomposites were studied by Lee and co-workers [21] and found that the clay content and silane content were the dominating factors in determining the individual water-vapour permeability. The relative vapour permeability of nitrile rubber nanocomposites containing ten parts of layered silicates were analysed by Hwang et al. [22] and noticed considerable reduction in vapour permeability in comparison with pure NBR. Effect of the aspect ratio of silicate platelets on the mechanical and barrier properties of hydrogenated acrylonitrile butadiene rubber (HNBR)/layered silicate nanocomposites was studied by Gatos et al [23] and found that the organo-fluorohectorite created a more extended tortuous path against gas penetration compared to organo-montmorillonite.

The aim of the present study is to investigate the gas transport properties with a view to understand the impact of geometry variation of the filler on the gas transport property of the polymer matrix.

7.2 Results and discussion

7.2.1 Permeability measurements

The gas transport properties of nitrile rubber nanocomposites with fillers having different particle size and chemical nature were analyzed using oxygen and carbon dioxide gases. The permeability of these gases through different nitrile rubber nanocomposite membranes are shown in figures [7.1-7.8]. In all the cases it has been observed that the gas transport in layered silicate filled system is lower than the filled systems of particles of larger size. Figure 7.1 indicates the transport of oxygen gas
through nitrile rubber nanocomposites at 10 phr loading of various fillers in comparison with unfilled system.

![Figure 7.1 Permeability of oxygen gas through nanocomposites at 10 phr filler loading](image)

The addition of layered silicate in NBR increased the barrier property to a considerable extent. This can be attributed to the strong polymer/filler interaction resulting in a more tortuous path for the gas molecules to travel through the membranes. The incorporation of CP and TO fillers in the matrix could produce the barrier property enhancement only to a very small extent. This is due to the large size of the filler which resulted in a comparatively weaker interaction between the filler and the matrix. Figure 7.2 illustrates the permeability of carbon dioxide gas through the nanocomposite with different fillers at 10 phr loading.
Figure 7.2  Permeability of carbon dioxide gas through nanocomposites at 10 phr filler loading

In this case also a better barrier property enhancement was noticed for layered silicate filled system in comparison with CP and TO filled systems. This can be attributed to the effective matrix-filler interaction as a result of the high aspect ratio of the layered silicate. Figures 7.3 and 7.4 represent the variation of gas permeability with layered silicate filler loading. Diffusion rates of oxygen and carbon dioxide gases are considerably reduced with increase in filler content. The decreasing trend of gas permeability is more prominent with layered silicate filled systems which can be explained on the basis of the availability of surface area per unit volume of the filler to interact with the matrix.
Figure 7.3 Variation of carbon dioxide permeability with layered silicate loading

Figure 7.4 Variation of oxygen permeability with layered silicate loading

Maximum surface area is available only in the case of layered silicate which resulted in a more tortuous path. This is due to the large aspect ratio of the layered silicate in comparison with CP and TO fillers. But in the case of
more particulate filler the tortuous path is less which will allow easy escape of
gas molecule through the system. Substantial reduction in permeability with
increase in filler loading has been noticed with layered silicate filled system.
This is due to the increase in tortuous path created as a result of the presence of
layered silicate. The permeability variations in CP filled system at different
loading are shown in figures 7.5 and 7.6.

![Figure 7.5](image_url)

**Figure 7.5** Variation of oxygen permeability with calcium phosphate
filler loading

Compared to layered silicate filled samples the permeability
decrease is less which may be due to the less tortuous path created by CP
particles. The incorporation of TO in nitrile rubber matrix doesn’t bring
much change in permeability of oxygen and carbon dioxide gases. Figures
7.7 and 7.8 clearly indicate that even at 20 phr loading, the permeability
variation is not appreciable.
Figure 7.6  Variation of carbon dioxide permeability with calcium phosphate filler loading

Figure 7.7  Variation of oxygen permeability with titanium dioxide filler loading
Figure 7.8 Variation of carbon dioxide permeability with titanium dioxide filler loading

This is due to the considerable change in the geometry as well as chemically inert nature of the TO particles. The large particle size of TO could bring practically no interaction with the polymer matrix which facilitates the easy passage of the gas molecules through the composite matrix. The platelet structure of layered silicates has the ability to improve the barrier properties of polymer materials according to a tortuous path model in which a small amount of platelet particles significantly reduce the permeability of gases through the nanocomposite. It is found that the transport of gases through nanoclay-filled membranes is lower than that of unfilled and macro filled samples. The enhancement in gas barrier properties of layered silicate reinforced membranes indicates strong polymer/filler interaction. This is perhaps due to the
formation of H-bond between the \(-CN\) groups of polymer matrix and the 
\(-OH\) groups of the layered silicate. The increases in gas barrier properties 
of the membranes reinforced with layered silicates are due to the 
nanometric level dispersion of the organic and inorganic phases [14]. The 
molecular-level polymer/filler interaction results in the reduced 
availability of free volume, and as a result, the permeability of filled 
membrane decreases. The enhanced gas barrier property of nanofilled 
membranes is due to the platelet-like morphology and high aspect ratio of 
fillers. Due to the high aspect ratio of layered silicates, the contact area 
between the filler and the matrix increases. Schematic representation of 
the tortuous path model is given in figure 7.9.

**Figure 7.9** Sketch of the path travelled by gas molecule through nitrile 
rubber nanocomposites having different filler geometry

From this it is clear that the gas molecules have to travel through a 
more tortuous path in the presence of layered silicate in comparison with 
CP and TO fillers. The gas permeability decreases with the addition of 
filler due to the increase in tortuous path formation. The structural 
peculiarity of the filler is another reason for the considerable enhancement
of gas barrier properties of nitrile rubber nanocomposites with the addition of layered silicate. Because of the absence of layered structure in CP and TO, the gas barrier property enhancement is very little. This will permit easy escape of gas molecule through the membrane. This is why gas permeability values of TO filled system are almost same as that of unfilled sample. The above observations can be correlated with the free volume data obtained from PALS measurements. The availability of free volume due to the restricted segmental mobility as a result of filler addition decreases in order NBR/TO>NBR/CP>NBR/LS.

7.2.2 The permselectivity factor

Based on the permeability studies it is possible to get selectivity factor which is an important aspect in membrane chemistry because of various applications of polymer membranes in different fields. The polymer membranes are usually used for the separation of gases and are based on the permeability and high selectivity of the desired gas. The essential requirement of an ideal membrane is high permeability along with high permselectivity. The permselectivity of a membrane is given by the equation [14]

$$\tau(CO_2; O_2) = \frac{P_{CO_2}}{P_{O_2}}$$

(1)

where $\tau$ is the permselectivity of a membrane towards $O_2$ and $CO_2$. $P(O_2)$ and $P(CO_2)$ are the permeability values of oxygen and carbon dioxide gases respectively and the values are plotted in figure 7.10.
Figure 7. 10  Carbon dioxide to Oxygen selectivity values of nanocomposites at 10 phr filler loading

The layered silicate filled system exhibited higher selectivity compared to CP and TO filled systems. This can be attributed to the effective NBR-filler interaction as result of the higher aspect ratio of the layered silicate. This effective interaction restricts the segmental mobility thereby reducing the free volume.

7.2.3 Positron annihilation lifetime spectroscopic analysis

It is necessary to study the percentage of free volume present in nanocomposite systems in order define the performance of the membrane. Positron annihilation lifetime spectroscopic analysis (PALS) is employed for the determination of free volume and this method helps to estimate the hole size at a nanoscale dimension. The transport of permeant through polymeric membranes can be described by two theories, namely, molecular and free volume theories. According to free volume theory the diffusion is not a thermally activated process as in molecular model but it
is assumed to result from random redistributions of free volume voids within a polymer matrix. Cohen and Turnbull [24, 25] developed the free volume models that describe diffusion process when a molecule moves into void larger than a critical size $V_c$. Voids are formed during the statistical redistribution of free volume within the polymer. Ito and co-workers [26] examined the relationship between the oxygen permeability and the free volume for ethylene–vinyl alcohol copolymer as the ethylene content varies, which significantly followed the free volume theory. Nagel et al. [27] correlated the free volume and transport properties of highly selective polymer membranes. Several researchers studied the impact of nanoparticles on the free volume and the barrier properties, and concluded that the permeability of nanocomposite was mainly influenced by the availability of fractional free volume [14, 28]. The change in o-Ps lifetime ($\tau_3$), o-Ps intensity ($I_3\%$) and relative fractional free volume percentage as a result of the addition of fillers are listed in Table 7.1

**Table 7.1** PALS measurement data of the nanocomposites (10 phr)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative fractional free volume (%)</th>
<th>o-Ps life time, $\tau_3$ (ns)</th>
<th>o-Ps intensity, $I_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>15.41</td>
<td>2.01</td>
<td>14.73</td>
</tr>
<tr>
<td>NBR/LS</td>
<td>7.84</td>
<td>1.77</td>
<td>11.33</td>
</tr>
<tr>
<td>NBR/CP</td>
<td>11.73</td>
<td>1.85</td>
<td>12.27</td>
</tr>
<tr>
<td>NBR/TO</td>
<td>13.20</td>
<td>1.92</td>
<td>14.41</td>
</tr>
</tbody>
</table>

It has been seen that the relative fractional free volume of unfilled polymer decreased upon the addition of fillers. The minimum relative fractional free volume percentage has been observed in the case of layered silicate filled system. This can be attributed to the interaction between layered silicates and polymer due to the platelet structure and high aspect
ratio of layered silicates. This will result in the restricted mobility of the chain segments in the presence of layered silicates. This results in a reduced free volume concentration or relative fractional free volume. But in the case of CP and TO filled systems, the availability of surface area is minimum to be interacted with the polymer matrix. Hence the segmental mobility of the matrix cannot be very much restricted. This is the reason why NBR/CP and NBR/TO samples showed weak barrier property in comparison with NBR/LS system.

**7.3 Conclusion**

- Nanocomposites with layered silicate showed reduced gas permeability in comparison with CP and TO filled systems. This could be attributed to very high aspect ratio of the layered silicate that resulted in a better matrix-filler interaction.

- An increase in filler loading could enhance the barrier property considerably in the case of layered silicate filled system. But the same trend was very weak with CP and TO filled system.

- Carbon dioxide showed higher gas permeability in comparison with oxygen gas.

- The free volume measurements revealed that layered silicate filled system could provide minimum free volume and hence showed good barrier property.

- The decrease in free volume may be due to the enhanced availability of surface area per unit volume of the filler, which can hinder the penetration of the gas molecules through the filled membrane.
References


