CHAPTER 1

Introduction

Abstract

Transport phenomena through polymeric membranes have been the subject of intensive research for the past several years. A better understanding of transport phenomena through polymers is highly important in order to achieve significant improvement in the areas of protective coatings, membrane separation processes and packaging of foods and beverages. Membrane separation techniques have been widely used for many industrial applications like desalination of brine and oxygen enriched air. Pervaporation, another important technique, has been widely used for the separation of a wide variety of organic liquid mixtures. In this chapter, the fundamentals of transport phenomena and the factors governing the transport of molecules through polymeric networks are discussed. The general features of pervaporation, vapour and gas transport are presented. A detailed review of current research in this field is also included. Finally the aim and scope of the present investigation are discussed.
Polymeric materials have the ability to dissolve molecules of gas, vapour, liquid and sometimes solute and to allow the transport of these molecules through the solid phase. This is in marked contrast to metals, glasses and ceramics, which are essentially impermeable [1]. Polymer films are widely employed as protective barriers, for example, metals are painted to prevent corrosion, paper is coated to render it moisture resistant, or foods are packaged to reduce the rate of deterioration. In these applications, the permeability of the film can be a major consideration. The plastics industry, in particular, has devoted considerable effort to improve the barrier properties of packaging materials. The design of economically viable barrier materials and membranes necessitates studies on the transport properties of various penetrants in polymers. Research in this area has been quite active and interesting reports on the interaction of polymer membranes with different liquids exist in the literature [2-32].

Polymers, during their life time are exposed to a variety of hostile chemical environments. The knowledge of the performance of polymers in the environment of hazardous solvents, vapors and temperature is essential for their successful applications as structural engineering materials. An understanding of the transport phenomena of the polymers plays a vital role in the application of the same as protective barriers in chemical and food industries, in membrane separation process, in the separation of solvent mixtures, in biomedical applications etc. [33-37]. Regenerated cellulose or cellophane was the first practical glassy film to find large-scale use in packaging [38]. The packaging of fruits and vegetables requires inward permeation of CO$_2$ and respiration of oxygen without loss of water [39]. In meat-wrap and cheese-wrap applications, the polymer films chosen are those which will allow at least certain minimum oxygen diffusion from air and minimize flavour loss respectively. The use of polymer membranes as liners and storage tanks for hazardous liquids is increasing [40].
Knowledge of the relation between the sorption properties and molecular structure of the polymer is essential for designing highly efficient end use products from polymers.

In the field of chemical engineering, polymer films are often used to effect the separation of mixtures (e.g., the extraction of helium from natural gas, the drying of solvents and the desalination of sea water [41]. In biomedical applications also polymeric membranes are extensively used. Polymer films serve, by selective diffusion, to remove certain components from blood when a damaged kidney can no longer do so. The components to be removed are urea, uric acid, water, creatine, phosphates and excess chlorides from blood through the membrane [42]. Polymer films can also be used to control the rate at which a substance is released into its environment. This property is exploited by the pharmaceutical industry in the production of sustained release dosage forms [43] and a good example is the ‘cold cure’ capsule, which contains tiny drug-containing polymer particles. The thickness of the polymer coat controls the rate at which the drug is released from the particle. Several components can be included in one capsule and each can be released at varying rates to give the optimum therapeutic effect. In recent years, new polymers have entered the area of controlled drug release. Many of these materials are designed to degrade within the body; among them are polylactides, polyglycolides, poly (lactide-co-glycolides), polyanhydrides etc. There are three primary mechanisms by which active agents can be released from a delivery system: diffusion, degradation and swelling followed by diffusion. Any or all of these mechanisms may occur in a given release system. An ideal drug delivery system should be inert, biocompatible, mechanically strong, comfortable for the patient, capable of achieving high drug loading, safe from accidental release, simple to administer and remove and easy to fabricate and sterilize.
Recently great attention has been focused on separation science and technology, which necessitates the studies of diffusion, sorption and permeation of various penetrants through polymeric membranes. A combination of improved economics and better technology has resulted in the enhanced commercial use of membranes for liquid and gas separations. The advantages of membrane separation over conventional processes are reduced capital cost, lower energy consumption, smaller and light weight and lower installation costs due to its modular design and simplified operation [44]. Membrane separation techniques have already been used in some industrial applications like the desalination of brine, salt manufacturing from sea-water and oxygen-enriched air [45]. Another important technique is pervaporation which finds application in industry for the separation of a wide variety of organic liquid mixtures [46,47]. In order to establish pervaporation as a competitive separation process, research has been concentrated on the development and optimization of polymeric membranes and their interaction with different penetrants. For water desalination by reverse osmosis, the most successful polymer membrane is Loeb-Sourirajan membrane (a cellulose acetate based membrane) [48]. The ultra thin layer (0.3 micron) gives excellent salt rejection, and because it is so thin, water diffusion rates are relatively high. For these types of membranes, it would be advantageous to have a high permselectivity and a high diffusion rate.

In engineering applications, the barrier properties of polymeric materials are often determined by the chemical structure of the chain and the system morphology. The parameters derived from chemical structure, such as degree of polarity, interchain forces, ability to crystallize and chain stiffness are essentially determined by the selection of the particular polymer. Dimensional stability and integrity of the polymeric materials in the presence of aggressive liquid environments is essential for their successful application. In order to design and make highly efficient and economically
viable barrier materials and membranes, the elucidation of the relationship between transport properties and molecular structure of polymers are necessary.

1.1 Historical Background

The first reported transport phenomena in polymeric materials was that of Graham [49], who in 1829 reported that a wet pig bladder inflated when placed in an atmosphere of carbon dioxide. The discovery that a rubber membrane is permeable to gases was made by Mitchell [50] in 1831. He showed that the rate of permeation varied for different gases and that the gases that permeated most rapidly were those most easily condensed and most soluble in water and other liquids. These ideas were developed by Graham [51] who later described the permeation process similar to that accepted today. He drew attention to the greater similarity of rubber to the liquid rather than the solid state and postulated that permeation was a three-stage process comprising condensation and solution at one face of the film, diffusion as a liquid to the other face, followed by dissolution and evaporation. The increasing rate of permeation with temperature was attributed by him to an increase in the softness of liquid nature of the rubber.

Subsequently, the need for materials with ever improved permeation properties has grown unabated. Detailed historical accounts have been given by Stannett [52] and Felder and Huvard [53]. These developments could not have taken place without an enhanced understanding of the factors which influence the permeation properties of the polymers involved. Significant advancements were made in this field in the past few years and it is still increasing.

1.2 Fundamentals of Transport Phenomena

The transport of penetrants through a polymer matrix can be explained in terms of diffusion, permeation and sorption phenomena. Diffusion of a small molecule through a polymer membrane occurs due to the random motions of
individual molecules. The transport mechanism in polymers consists of three steps: (1) adhesion of penetrant species on the surface of the matrix, (2) diffusion of the penetrant species through the matrix, and (3) desorption of the penetrant species from the matrix. A schematic representation of the transport mechanism in polymers is shown in Figure 1.1.

**Figure 1.1:** Schematic representation of transport mechanism:
- (1) Adhesion of species on the surface of the matrix
- (2) Diffusion of species through the matrix
- (3) Desorption of the species from the matrix

The transport process slowly tries to equalize the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane. This process can be described by Fick's first and second laws of diffusion.

If a concentration gradient is established across some arbitrary reference section in the polymer, a net transport of penetrant occurs in the direction of decreasing concentration. This phenomenon can be described in terms of Fick's first law of diffusion according to which the diffusive flux, $J$ (the amount of penetrant passing through a plane of unit area normal to the direction of flow during unit time) in the $x$-direction of flow is proportional to the concentration gradient $\frac{\partial c}{\partial x}$ as
\[ J = -D \frac{\partial c}{\partial x} \]  \hspace{1cm} (1.1)

where \( D \) is the diffusion coefficient and \( c \) the concentration of the diffusing molecule. This equation is applicable when the diffusion is in the steady state, i.e., when the concentration does not vary with time.

On the other hand, Fick’s second law describes the unsteady state transport process, which is given by the rate of change of the penetrant concentration at a plane within the membrane, as

\[ D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \]  \hspace{1cm} (1.2)

This is an ideal case in which the membrane is isotropic and \( D \) is independent of distance, time and concentration. Depending on the boundary conditions, there are many solutions available for Equation (1.2).

When the diffusion rate \( J \) achieves a steady value (no longer varies with time) a material balance requires that it also be independent of \( x \), in which case Equation (1.1) can be integrated to give,

\[ \int_0^h Jdx = - \int_{c=c_0}^{c=c_2} D(dc) \]  \hspace{1cm} (1.3)

\[ J = - \frac{1}{h} \int_{c=c_0}^{c=c_2} D(dc) \]  \hspace{1cm} (1.4)

Equation (1.4) indicates the steady-state diffusion rate which is inversely proportional to the overall membrane thickness \( h \) for a given set of boundary conditions. To complete the integration, the variation of \( D \) with \( c \) must be known. In some systems, the diffusion coefficient does vary with concentration because the Van der Waals forces are high between the
diffusing molecules themselves and between the diffusing molecules and the polymer chains.

When there are relatively weak intermolecular forces of attraction between the diffusing molecules and the polymer chains, the solubility is low and the polymer structure is not significantly altered. Under these circumstances $c$ can vary without affecting $D$, and Equation (1.4) then becomes

$$J = -\frac{D}{h} (c_2 - c_1)$$

(1.5)

where $c_2$ and $c_1$ are respectively the concentrations of the diffusing molecules dissolved at the downstream and upstream polymer-membrane faces. In many cases, it is the pressures or partial pressures $p$ of a gas or vapour above the faces of the polymer film, rather than the surface concentration, which are known. These quantities are related by Henry’s law, which states that

$$C = S p$$

(1.6)

where $S$ is the solubility constant for a given gas-polymer system.

The combination of Equations (1.5) and (1.6) gives the well-known permeation equation,

$$J = DS \left[ \frac{p_1 - p_2}{h} \right]$$

(1.7)

The product $DS$ is called the permeability coefficient, $P$, so that

$$P = D S$$

(1.8)

In terms of permeability, the flux equation (1.7) can be written as

$$J = P \left[ \frac{p_1 - p_2}{h} \right]$$

(1.9)
1.3. Factors Affecting the Transport Process

The important factors, which influence the transport process, are briefly discussed in the following section.

1.3.1. Nature of the polymer

The transport behaviour of a given penetrant varies from one polymer to another. Transport properties depend on the free volume within the polymer and on the segmental mobility of the polymer chains. The segmental mobility of the polymer chains is affected by the extent of unsaturation and crosslinking, degree of crystallinity and nature of substituents. In general, dense polymer membranes have no pores but there exists the thermally agitated motion of chain segments to generate penetrant scale transient gaps in the matrix (free volumes) allowing penetrants to diffuse from one side of the membrane to the other side [54]. A larger amount of free volume is basically readily accessible for diffusion in amorphous polymer matrices due to internal micro-motions of chain rotation and translation, as well as vibration. On the other hand in the glassy state, there is restricted chain mobility. Variation of permeation coefficient with fractional free volume is given in Figure 1.2 [55]. Rotation about the chain axis is limited and motion within the structure is largely vibratory within a frozen quazi-lattice. These types of polymers have very dense structures, with very little internal void space. Ponangi et al. [56] investigated free volumes of four different polyurethane membranes Spandex, BFG-1, BFG-2 and BFG-3 by organic vapour diffusion. The computed diffusion coefficient and free volume at 30°C in benzene are given in Table 1.1. It is clear from the table that the diffusion coefficient value decreases with decrease in average fractional free volume values.
Figure 1.2 Plots of permeation coefficient vs. Fractional free volume for nylon-6-clay nanocomposite/PVA blend specimens [55]

Table 1.1. Comparison of diffusion coefficient and free volume (Penetrant: benzene vapour at 30°C) [Ref. 56]

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>$D \times 10^{-7}$ (cm$^2$/s)</th>
<th>Average fractional free volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spandex</td>
<td>7.14</td>
<td>0.0634</td>
</tr>
<tr>
<td>BFG-1</td>
<td>2.45</td>
<td>0.0562</td>
</tr>
<tr>
<td>BFG-2</td>
<td>0.905</td>
<td>0.04804</td>
</tr>
<tr>
<td>BFG-3</td>
<td>0.611</td>
<td>0.03868</td>
</tr>
</tbody>
</table>

The glass transition temperature (Tg) of the polymer has a marked influence on the transport properties. Polymers with low glass transition temperature possess greater segmental mobility and will have higher diffusivity. Lee et al. [57] studied the gas barrier properties of alkylsulfonylmethyl-substituted poly (oxyalkylenes). Oxygen permeability coefficients of three methylsulfonylmethyl-substituted poly(oxyalkylene),
poly[(oxy(methylsulfonylmethyl)ethylene] (MSE), pol[y(oxy(methylsulfonylmethyl) ethylene-co-oxyethylene] (MSEE), and poly[oxy-2,2-bis(methylsulfonylmethyl) trimethylene oxide] (MST) were measured. Among the three polymers studied, the permeabilities vary in the order MST>MSEE>MSE, probably because steric hindrance between the side chains made the chain packing inefficient. As the side chain length of poly [oxy (alkylsulfonyl-methyl) ethylene] increased, Tg and density decreased and the oxygen permeability coefficients increased. The effect of polymer density on diffusion was studied by Auerbach et al. [58] by using octadecane as the penetrant. They have reported a three-fold decrease in the diffusion coefficient for octadecane through polyisoprene, as the residual unsaturation was decreased from 100 to 37% by hydrogenation. This is due to the restriction in segmental mobility by hydrogenation.

Van Amerongen [59] studied the diffusion and permeability of hydrogen, helium, nitrogen, oxygen, acetylene and cyclopropane through a series of natural and synthetic rubbers and observed that samples containing larger number of substituent methyl groups had lower diffusion and permeability coefficients. He observed an inverse relationship between nitrile content and sorption coefficient in a series of butadiene / acrylonitrile copolymers (Figure 1.3).
Bulky groups in the polymer chain effectively reduce their segmental mobility and thereby diffusion ability. The polymers containing this type of groups in the chains increase their $T_g$. The $T_g$ values of polyethylene (PE) and polypropylene (PP) are -20 and +5°C respectively. PE has flexible backbone but in the case of PP, there are -CH$_3$ groups to inhibit the freedom of rotation [60]. Strong polar attraction and crystalline regions also contribute to high $T_g$ values. Table 1.2 demonstrates that for polymers with the same substitution pattern, it is the flexibility of the backbone that determines permeation properties [61].

The Si-O backbone allows for rapid chain segmental motion to occur in the silicone rubber (polymer C) and substitution of the Si-O linkage by Si-CH$_2$ (polymer B) dramatically reduces the permeability to a value even less than that of butyl rubber (polymer A). The insertion of a (CH$_2$)$_n$ sequence into a siloxane backbone (polymer D) also leads to a decrease in permeability. Similarly, the Si-O backbone substitution of methyl by more bulky substituents decreases the permeability (polymer E). These
decreases in permeability are mainly due to a decrease in permeant diffusivity, caused by an increasing rigidity of the polymer backbone and a decreasing free volume available for the diffusion of the penetrant molecules. The substitutions of bulky functional groups in the side chains appear to have a greater influence on decreasing diffusivity than substitution of these groups in the polymer backbone [61-63].

Table 1.2: Effect of side chain and main chain substitution on oxygen permeability [Ref. 61]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g (^0 \text{C}) )</th>
<th>( P \times 10^{-17} ) (mol m(^{-1}) s(^{-1})Pa(^{-1})) (at 35(^0)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-CH(_2)CMe(_2)-</td>
<td>-76</td>
</tr>
<tr>
<td>B</td>
<td>-CH(_2)SiMe(_2)-</td>
<td>-92</td>
</tr>
<tr>
<td>C</td>
<td>-CSiMe(_2)-</td>
<td>-123</td>
</tr>
<tr>
<td>D</td>
<td>( \text{Me-Si((\text{CH}_2)\text{Me})_8-SiMe} )</td>
<td>-88</td>
</tr>
<tr>
<td>E</td>
<td>( \text{Ph-SiO-Me} )</td>
<td>-28</td>
</tr>
</tbody>
</table>

The water sorption behaviours of biphenyl tetracarboxylic dianhydride (BPDA) based polyimide thin films depending upon the structural isomers of diamine were studied by Seo and co-workers [64] and is shown in Table 1.3. The polyimide films with para oriented linkages in backbone structure showed relatively lower diffusion coefficient and water uptake than the corresponding polyimide films with meta oriented linkages because of the well developed crystalline structure and good intermolecular chain ordering.
Table 1.3: $T_g$, Diffusion coefficient and water uptake of the BPDA based polyimide thin films [Ref. 64]

<table>
<thead>
<tr>
<th>Polyimide Structure</th>
<th>$T_g$ (°C)</th>
<th>$D \times 10^{-10}$ (cm$^2$/s)</th>
<th>Water uptake (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPDA – p PDA</td>
<td>360</td>
<td>1.6</td>
<td>1.52</td>
</tr>
<tr>
<td>BPDA – m PDA</td>
<td>375</td>
<td>7.4</td>
<td>4.75</td>
</tr>
<tr>
<td>BPDA – p’p’ ODA</td>
<td>295</td>
<td>3</td>
<td>1.62</td>
</tr>
<tr>
<td>BPDA – p’m’ ODA</td>
<td>300</td>
<td>6.7</td>
<td>2.32</td>
</tr>
<tr>
<td>BPDA – p’p’ DDS</td>
<td>400</td>
<td>7.2</td>
<td>5.14</td>
</tr>
<tr>
<td>BPDA – p’m’ DDS</td>
<td>330</td>
<td>12.4</td>
<td>5.25</td>
</tr>
</tbody>
</table>

The permeability of permeants which interact weakly with functional groups present in a polymer can be expected to decrease as the cohesive energy of the polymer increases. For example, by increasing the polarity of the substituent group on a vinyl polymer backbone, oxygen permeability is reduced by almost 50,000 times, as shown in Table 1.4.

Table 1.4: Effect of functional groups on oxygen permeability of vinyl polymers (CH$_2$CHx)$_n$ [Ref. 65]

<table>
<thead>
<tr>
<th>Functional group</th>
<th>$P \times 10^{-17}$ (mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.3</td>
</tr>
<tr>
<td>Ph</td>
<td>1.1</td>
</tr>
<tr>
<td>Me</td>
<td>0.397</td>
</tr>
<tr>
<td>F</td>
<td>0.0396</td>
</tr>
<tr>
<td>Cl</td>
<td>0.021</td>
</tr>
<tr>
<td>CN</td>
<td>1.08 x 10$^{-4}$</td>
</tr>
<tr>
<td>OH</td>
<td>2.64 x 10$^{-5}$</td>
</tr>
</tbody>
</table>
1.3.2. Nature and distribution of crosslinks

The transport properties of the same polymer at the same crosslink density depend on the nature of the crosslinks. Poh et al. [66] have studied the sorption behaviour of bulk and solution crosslinked natural rubber (NR) networks prepared by irradiation with gamma rays. They found that in benzene, solution crosslinked networks swell more than the corresponding bulk crosslinked networks having the same crosslink density. The transport properties of polymers are strongly dependent on the distribution of crosslinking in them. An uncrosslinked polymer will usually dissolve in an appropriate solvent. By contrast, crosslinked polymers will not dissolve. Solvation of chain segments cannot overcome the effect of the covalent bonds between the macromolecules; hence crosslinked molecules cannot be carried off into the solution. Depending on the distribution of crosslinks or crosslink density, however, such materials may admit significant amounts of solvent, becoming softer and swollen as they do so. The swelling by fairly lightly crosslinked materials is generally reversible and, given appropriate conditions, solvent that has entered a crosslinked structure can be removed and the polymer can be returned to its original size [61]. Heavily crosslinked polymers have a dense three-dimensional network of covalent bonds in them, with little freedom for motion by the individual segments of the molecules involved in such structures. The mass transport process is very tortuous in these types of polymer matrices.

In membrane technology, there are two reasons for crosslinking a polymer. The first reason is to make the polymer insoluble for the feed mixture and the second is to decrease the degree of swelling of the polymer in order to maintain selectivity [67]. Staudt-Bickel and Koros [68] improved the selectivity of polyimide membranes for CO$_2$/CH$_4$ mixture by chemical crosslinking with ethylene glycol. CO$_2$/CH$_4$ selectivity increased with an increase in the degree of crosslinking because of reduced swelling and
polymer chain mobility. The CO$_2$ permeability was not significantly lowered by using ethylene glycol as a crosslinking agent since the additional free volume caused by the crosslinks compensated the reduced chain mobility.

1.3.3. Effect of plasticisers

The addition of plasticisers to a polymer results in increased segmental mobility and hence an increased penetrant transport. Arvanitoyannis et al. [69] investigated the CO$_2$ water vapour permeabilities of chitosan/poly (vinyl alcohol) (PVA) blends plasticized with sorbitol and sucrose. They found that the permeability values increased with an increase in plasticizer content. Sorption and diffusion of oxygen in plasticized ethyl cellulose films of varying degrees of substitution were studied by Beck and Tomka [70]. It was found that as the plasticizer concentration and temperature increased, the permeability coefficient also increased.

1.3.4. Nature of the penetrants

The transport process through polymers depends very strongly on the size, shape, phase and molecular weight of the penetrants. An increase in size in a series of chemically similar penetrants generally leads to a decrease in their diffusion coefficients due to the increased activation energy needed for diffusion. The decrease in diffusivity with increase in size of the penetrant has been reported by many investigators [71,72]. Harogoppad and Aminabhavi [73] studied the effect of long chain aromatic hydrocarbon diffusion through different rubbery polymers. The dependence of diffusion coefficient and other related parameters on the size and shape of the penetrant molecule has been discussed. It was found that the transport parameters decreased with an increase in penetrant molecular size. Hong [74] investigated the effect of solvent size on the diffusion process for various solvents with NR and polybutadiene (PB) in terms of the free-volume theory.
Permeant shape also has a significant effect on the transport process. For example, flattened or elongated molecules have higher diffusion coefficients than spherical molecules of equal molecular volume [75]. In general, permeant size and shape effects are much more marked in glassy polymers than in rubbery polymers. This arises from the differences in the penetrant-polymer mixing process. In rubbery polymers, energy is required to generate sites for the penetrant molecules to occupy but since increasing permeant size tends to increase the heat of sorption, it follows that larger penetrant molecules will be readily sorbed leading to enhanced plasticization of the polymer chains. As a result of this, the smaller penetrants will have a greater diffusion coefficient, the polymer will be less plasticised, whereas the lower diffusion coefficient of the larger penetrants will be compensated for by the higher degree of sorption. Figure 1.4 shows the effect of size of penetrants on the mol% uptake of thermoplastic polyurethane (TPU)/NR blend membranes at 30°C [30].

Figure 1.4: Mol% uptake of benzene, toluene and xylene by 20/80 TPU/NR blend at 30°C [Ref.30]
The permeant phase also influences the transport process. The permeation of condensable vapours or liquids is generally much faster than that of permeant gases. Permeants, which are good solvents for the polymer, swell and plasticize the polymer structure, which gives rise to an increased mobility of the polymer chain segments leading to enhanced permeation rates. For example, the permeability in a poly (butadiene-co-acrylonitrile) rubber (NBR) increases seven times on varying the permeant from gaseous nitrogen to liquid methyl ethyl ketone [76].

1.3.5. Fillers

Depending upon the degree of adhesion and compatibility of the fillers to the polymer matrix, permeability of a particular penetrant may either increase or decrease. When inert filler which is compatible with the polymer matrix is used, it will take up the free volume within the polymer matrix and create a tortuous path for the permeating molecules [77]. The degree of tortuosity is dependent on the volume fraction of the filler and the shape and orientation of the particles. When the filler is incompatible with the polymer, voids tend to occur at the interface, which leads to an increase in free volume of the system and consequently, to an increase in permeability. Priya Dasan et al. [78] investigated the influence of carbon black filler on the transport of aromatic hydrocarbons (benzene, toluene and xylene) through the Poly(ethylene-co-vinyl acetate) (EVA) matrix. They have used three different types of carbon black, viz, semi-reinforcing furnace (SRF), high abrasion furnace (HAF) and intermediate super abrasion furnace (ISAF). They found that the solvent uptake reduced by carbon black incorporation. Among the filled samples studied, the ISAF filled sample showed the lowest uptake followed by HAF and then SRF filled samples. The low solvent uptake behaviour of ISAF is attributed to its low particle size and the greater reinforcement with the studied matrix.
Figure 1.5 shows the effect of filler loading on the mol% uptake of NR/EVA blend at 26°C [79].

![Sorption curves of pure NR, 60/40 NR/EVA and 60/40/30 NR/EVA/ISAF in benzene at 26°C](image)

**Figure 1.5:** Sorption curves of pure NR, 60/40 NR/EVA and 60/40/30 NR/EVA/ISAF in benzene at 26°C [Ref. 79].

Solvent resistance properties of nano-structured layered silicates filled 70/30 latex blend of NR and carboxylated styrene butadiene rubber (XSBR) were investigated by Ranimol et al. [80,81] using benzene, toluene and p-xylene with reference to the effects of penetrant size and filler loading. Sodium bentonite and sodium fluorohectorite were used as fillers for their investigation. Due to the lack of polymer-filler interaction, the aggregation of filler particles has been found to be higher in NR. The filled samples showed a reduced swelling rate owing to the tortuosity of the solvent path. The studies by Sombatsompop and Kumnuantip [82] experimentally monitored the toluene penetration properties through NR/carbon black/reclaimed rubber blends vulcanized by microwave (MW) irradiation and conventional thermal (CT) systems. The results suggested that the vulcanizates from the MW method had higher resistance toluene penetration than those from the CT method. The differences in the results
between these two curing systems were explained in terms of the density and the type of crosslinks present in the vulcanizates.

Equilibrium swelling in solvents was found to be a very good technique for assessing rubber-fibre adhesion in fibre filled composites. Lowering of equilibrium swelling in fibre filled samples indicates excellent fibre-rubber adhesion. Haseena et al. [83] examined the interfacial adhesion of short sisal/coir hybrid fibre reinforced NR composites by restricted equilibrium swelling technique. As fibre content increases, the solvent uptake has been found to decrease due to the increased hindrance and good fibre-rubber interaction. Due to the improved adhesion between the fibres and NR, the ratio of the volume fraction of rubber in dry composite samples to that in swollen samples has also been found to decrease.

The gas transport properties of nanoclays (organomodified montmorillonite and sepiolite) and carbon nanofiber filled SBR films were investigated by Bhattacharya et al. [84] using O$_2$ as the permeant. Figure 1.6 shows the oxygen transmission rate (OTR) values of Cloisite15A filled SBR nanocomposites at different loadings of Cloisite at 30$^\circ$C. By virtue of enhanced polymer/filler interaction and consequential lowering of free volume and polymer mobility, the nanocomposites exhibited lower permeability to oxygen. The higher polymer/filler interaction is associated with the structure and morphology of these high aspect ratio nanofillers. In depth studies on the morphology further highlighted the role of polymer-filler interaction on the enhancement of barrier properties.
Kang et al. [85] studied the molecular transport in composite membranes with tubular fillers. Nanotubes were incorporated into polymeric membranes for molecular separations. It is found that the filler volume fraction, as opposed to the filler orientation, intrinsic permeability, and aspect ratio, has the most significant impact on the membrane permeability. Hanson et al. [86] investigated the effects of nanoparticles on the rates of gas diffusion through glassy polymers by a combination of molecular dynamics and kinetic Monte Carlo techniques. Using such a methodology, the effect of fullerene nanoparticles upon the diffusivities of N\textsubscript{2} and CO\textsubscript{2} in a polystyrene matrix was investigated. The addition of nanoparticles was found to cause a lowering of the diffusion coefficients of both N\textsubscript{2} and CO\textsubscript{2}.

Figure 1.6. OTR values of Cloisite 15A/SBR nanocomposites at different loadings of cloisite 15A at 30\textdegree C [Ref. 84]
1.3.6. Temperature

The permeability $P$ of permeants through an amorphous, homogeneous, dense film increases with temperature, according to Arrhenius relationship:

$$P = P^\star \exp \left[ - \frac{E_p}{RT} \right]$$

(1.10)

where $E_p$ denotes the activation energy of permeation. $E_p$ is the sum of the activation energy of diffusion, $E_d$, and heat of sorption $H_s$.

$$E_p = E_d - H_s$$

(1.11)

Diffusion through polymers is an activated process; therefore, diffusion coefficients always increase with temperature that is $E_d$ is always positive. Increase in temperature increases polymer segmental mobility and also kinetic energy of the penetrant thereby generally increasing penetration rate. Figure 1.7 shows the influence of temperature on the sorption behaviour of EVA/Clay nanocomposites [87].

![Figure 1.7. Influence of temperature on the sorption behaviour of EVA/clay nanocomposite [Ref.87].](image)
1.3.7. Polymer molecular weight

The effect of molecular weight on transport properties is generally found to be low. As the polymer molecular weight increases, the number of chain ends decreases. The chain ends represent a discontinuity and may form sites for permeant molecules to be sorbed into glassy polymers. Berens and Hopfenberg [88] studied the diffusion of several organic vapours (acetone, benzene etc.) through polystyrene (PS) films and found that the diffusivity was decreased by a factor of ten as the molecular weight increased from 10000 to 300000. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of different intrinsic viscosities has been studied by Chowdhury et al. [89] to understand the effect of polymer molecular weight on the permeability and permeability ratio of CO$_2$/CH$_4$ and O$_2$/N$_2$ gas pairs. The increase in permeability of dense films prepared from higher molecular weight PPO was explained in terms of increased free volume. Chakrabarty et al. [90] studied the effect of molecular weight of polyethylene glycol (PEG) on membrane morphology and transport properties.

1.3.8. Crystallinity and orientation

It is generally recognized that the gas or liquid permeating molecules can hardly diffuse through the crystalline regions but can only permeate through the amorphous regions of a polymer resin, because the amorphous regions offer enough space allowing permeating molecules to enter and diffuse. The crystalline areas in the crystalline polymers act as impermeable barriers to permeants and they force the permeant molecules to diffuse along longer path lengths. Brown et al. [91] investigated the diffusion and sorption of small molecules through amorphous and crystalline PB. They found that, in the case of amorphous polymers (trans content less than 70-80 %) the diffusion coefficient at zero penetrant concentration decreases with increasing trans content and at trans content above about 80%, a sudden drop in the diffusion coefficient occurs due to the onset of crystallinity.
In the case of crystalline polymers, the crystalline areas act as impermeable barriers to permeants and they force the permeant molecules to diffuse along longer path lengths. Excellent reports regarding the effect of crystallinity on the transport process exist in literature. Van Amerongen [92] using gutta percha as diffusion medium was among the first to demonstrate how the crystallization reduced the diffusion and permeation coefficients. Studies on the the gas transport behaviour of semi-crystalline syndiotactic polystyrene samples containing amorphous and crystalline parts were reported by Prodpran et al. [93]. The $O_2$ and $CO_2$ permeabilities were examined as a function of crystallinity. These measurements confirmed that more dense crystalline form was impermeable for the transport of small gas molecules while less dense crystalline form was highly gas permeable. Unusual gas transport behaviour of the crystalline form observed was attributed to the porous crystalline structure containing nano-channels.

Drieskens et al. [94] studied the effect of crystallinity on barrier properties of poly (lactic acid) (PLA). PLA is at present the most promising and commercially available bio-based and biocompostable plastic. The properties of PLA, however, are rather poor, notably its low glass transition temperature, its intrinsic low crystallization rate and the limited barrier properties with respect to water, oxygen and carbon dioxide in comparison with oil-based counterparts, notably polyesters (PET). A correlation is made between crystallization, various morphological parameters and the barrier properties of PLA. Crystallization of PLA causes a decrease of the oxygen permeability, but not in linear proportion with the decrease in amorphous volume. This has been explained in terms of the influence of the space filling and the inner crystalline structure on gas transport properties. Furthermore, the presence of a rigid amorphous fraction with lower density can have strong impact on PLA gas permeability, in particular on the gas solubility coefficient of PLA. Compan et al. [95] investigated the effect of crystallinity
on the gas transport in semicrystalline films based on linear low density polyethylene.

1.3.9. Effect of blending

Blending of two or more different polymers makes it possible to achieve various property combinations in the final material—usually in a more cost-effective way than in the case of synthesis of new polymers [96, 97]. Therefore great attention has been paid to the investigation of these systems, as well as to the development of specific materials with end applications in mind. Mixing of two polymers can produce either a homogeneous mixture at the molecular level (miscible blend) or a heterogeneous phase-separated (immiscible) blend. In homogeneous blends, the diffusion process is influenced by the interaction between the component polymers [98] while in heterogeneous blends; it is influenced by the interfacial phenomena and the rubbery or glassy nature of the phases [99]. However, most polymer blends are heterogeneous, and consists of a polymeric matrix in which the second polymer is embedded. As a result, the effects of permeability depends on the degree of heterogeneity of the system and therefore on the method of preparation [100]. The nature and type of polymers used (i.e. rubbery, glassy, hydrophilic or hydrophobic) are also important.

A systematic study on the sorption behavior of polymer blends was first studied by Cates and White [101]. Since then, the literature revealed a series of investigations on the transport behaviors of polymer blends. A detailed analysis of permeation data was done by Robeson et al. [102]. Although they studied the O$_2$ and N$_2$ permeability of block copolymers, their analysis stands as a model for a description of the nature of the continuous and dispersed phases in a blend. Segal et al [103] studied the sensing of liquids by electrically conductive immiscible PP/TPU blends containing carbon black. They found that the interphase region, its quantity, and continuity
played a significant role in the liquid-transport process. Dhamodharan et al. [104] investigated the properties of blends of EPDM and TPU to understand the compatibility and morphology. They found that the mechanical properties of unmodified EPDM blends improved with the addition of PU. Poomalai and Siddaramaiah [105] prepared and studied poly (methyl methacrylate) (PMMA) and TPU blends in different compositions. They observed that there is a slight improvement in thermal stability with an increase in TPU content in the blends. The diffusion properties of PU/poly(dimethylsiloxane) (PU/PDMS) blend membranes were studied by Lue et al. [31]. They found that the toluene solubility was highest in 20/80 PU/PDMS blend and methanol solubility increased with an increase in PU content.

1.4. Transport phenomena in different polymeric systems

1.4.1. Diffusion in rubbery polymers

Considerable attention has been focussed on the diffusion of permeants through the elastomer network in the past few years. The important features of rubbery polymers are unsaturation, segmental mobility and the large amount of free volume within the polymer. In general, the transport of vapours and liquids do not obey Henry’s law in rubbery polymers. Moreover, the diffusion coefficients are often highly dependent upon the concentration of the penetrant in the polymer. Fick’s diffusion laws and conventional equilibrium relationships describe the transport phenomena in rubbery polymers. Aminabhavi et al. [106] investigated the diffusion and sorption of a variety of organic liquids through rubbery polymers such as PU, neoprene (CR), SBR, EPDM, NBR and NR. The penetrants used were cyclic compounds, esters and hydrocarbons. The transport mechanism found to depend, to a great extent, on the type of the solvent molecule and the barrier material. In all the polymer-solvent systems, the activated diffusion mechanism was found to be operative and the computed transport parameters indicated smaller diffusion coefficients
and higher activation energies for bigger solvent molecules. The diffusion mechanism has been classified to be anomalous.

Several researchers used the equilibrium swelling technique for finding out the interaction of different fillers/fibres with elastomers. For example, Bakobza and Rapoport [107] studied the degree of reinforcement of carbon black and silica fillers in NR using diffusion technique. It is demonstrated that at intermediate strains, the increase in the moduli can be explained by the inclusion of rigid particles in the soft matrix and from molecular interactions between the rubber and the filler. The interactions have been evaluated by equilibrium swelling and by orientational measurements. Kulkarni et al. [108] investigated the sorption and diffusion behaviour of esters, aldehydes, ketones, and aromatic liquids through fluoelastomeric membranes and found that transport behaviour is not merely on the size of the penetrants but also on the nature of liquid molecules and membranes. These studies are extremely important for the design of new polymer materials, which would greatly benefit for the development of high performance membranes. Alentiev et al. [109] proposed a novel class of silicon-containing rubbers as membrane materials for the separation of hydrocarbons of natural and associated petroleum gas. Homo-polymers of general formulae –Si-(CH$_3$)$_2$-CH$_2$– and –Si-(CH$_3$)$_2$-CH$_2$-CH$_2$-CH$_2$– and copolymers with the same randomly alternating repeat units were prepared by thermal initiated polymerization of strained silicon-containing four-member cyclic compounds. The amorphous copolymers exhibited a combination of good film forming properties and relatively high permeability.

Kariduraganavar et al. [110] reported the sorption kinetics, diffusion and permeation of a series of n-alkanes through commercial TPE elastomer (FA 150L) at different temperatures. They have examined the effects of size of the penetrants on the sorption and diffusion behaviour of elastomer and found that the sorption coefficients decreased with
increasing size of penetrants. A detailed study of the transport behaviour of penetrants through different rubbery polymers has been reported by several researchers [111-116]. Rubbers generally follow Fickian mode of transport. However, there are cases where the sorption process shows deviation from the typical Fickian trend [117].

1.4.2. Diffusion in glassy polymers

Glassy polymers are characterized by hard and brittle moiety with restricted chain mobility and have very little void space (0.2-10%). Therefore diffusion in glassy polymers is more complex compared to that in rubbery polymers. Stannett and Hopfenberg [118] described the various glassy state transport anomalies, which include (a) time dependent boundary conditions for vapour transport (b) dual sorption modes even for inert gases (c) diffusion coefficients characterized by an apparent time dependence (d) polymer relaxations which provide the rate determining transport step (e) polymer fracture or micro-fracture (crazing) accompanying polymer relaxation and (f) a significant change in the transport mechanism as the \( T_g \) is traversed. A significant deviation from the normal or Fickian trend of transport is observed with glassy polymers [119,120]. Sun and Lee [121] examined the sorption and desorption of water vapour into and from a hydrophilic glassy poly (2-hydroxyethyl methacrylate) (PHEMA). Bove et al. [122] investigated the sorption and diffusion of dichloromethane vapor in amorphous poly(ethylene terephthalate) (PET) with the aim of studying how aging phenomena, at different temperatures, influence the transport properties. It has been found that aging produces the appearance of non-Fickian behavior in the sorption curves as well as the reduction of the diffusion coefficients.

A new system of saturated polyester and their nanocomposites synthesized from glycolyzed PET with varied composition is investigated for the sorption and diffusion studies in water by Katoch et al. [33]. The kinetics of sorption is studied by using the equation of transport phenomena. The
dependence of diffusion coefficient on composition and temperature has been studied for all polymeric samples. The diffusion coefficient in saturated polyester samples decreases with an increase up to 50% glycolyzed PET content. The diffusion coefficient increases with an increase in temperature for all polymer samples. The sorption coefficient shows a little change with variation in composition as well as temperature for all the samples. The activation energy for diffusion and permeation is positive for all the samples. The heat of sorption also was positive for all the samples, indicating Henry type mode of sorption. Detailed study of the transport behaviour of penetrants through different glassy polymers has been reported by several researchers [123-125].

1.5. **Membrane based transport process**

The development of membranes and its utilization for the separation of liquid and gas mixtures is an important emerging technique in membrane science and technology. Membrane technologies can be utilized to separate, fractionate and concentrate contaminants or process components. In general, they require minimal temperature changes and chemical addition, operate in either continuous or batch modes, consume significantly less energy than traditional separation processes and are easy to integrate into existing process due to their modular nature and compact size without altering the chemical structure of the processed materials. During the past two decades, industrial membranes are being developed for a wide variety of chemical separation application involving the treatment of industrial liquids, gases and vapours, such as those involved in waste water treatment [126], pollution control, water reuse and waste recovery, food processing, gas separations, petroleum engineering, biotechnology and biomedical devices [127-130]. Generally, membrane processes are classified based on various driving forces. Some use pressure difference (micro filtration, reverse osmosis and piezodialysis), while others use other
driving forces such as concentration difference (gas separation, pervaporation and dialysis) [131]. The feasibility and success of the transport process depend upon the nature of the membranes used.

1.5.1. Membranes

A membrane is a thin barrier that permits selective mass transport. Although membranes can be prepared from metals, ceramics, and microporous carbon, polymeric membranes have great versatility and are widely used. Membranes which are useful as selective barriers for the rectification of multicomponent gaseous or liquid feeds must provide high product throughputs with sufficient selectivity to permit the completion of the desired separation in a single stage. The membrane must also be chemically stable at the temperature and pH of the feed solution. Membranes must exhibit sufficient mechanical stability to permit normal handling during installation, use and maintenance. In addition to these, the selective membrane must be resistant to biological attack.

1.5.2 Types of membranes

As a first classification, membranes can be divided into two groups: biological and artificial membranes [132]. Artificial term can be applied to all membranes made by man with natural materials and with synthetic materials (synthetic membranes). Synthetic membrane can be divided further into organic (made up of polymers) and inorganic (made with metals, alumina etc.) membranes. Since the effectiveness of the membranes in applications depends on the detailed morphology and microstructures of membrane systems, another classification of synthetic membranes can be made as shown in Figure 1.8. [133]. Synthetic membranes can be classified as either symmetric or asymmetric. Symmetric membranes are comprised of one material of a single chemical composition and structural morphology. They are also called isotropic.
Asymmetric membranes are constituted of two or more structural planes of different morphologies, and the size of the pores changes from one surface of the membrane to the other. Asymmetric membranes are sometimes called anisotropic. Symmetric membranes can be classified into three groups

(a) homogeneous, dense membranes with an active layer thickness of more than 10µm; these membranes are often used for the study of polymer material science aspects in gas separation and pervaporation.

(b) cylindrical porous membranes which are normally used in small size laboratory experiments like enzyme and DNA separations from dilute solutions;

(c) sponge-like porous membranes; these membranes have normally an average pore size of 0.2-5µm and find applications in the filed of microfiltration.

**Figure 1.8:** Schematic representation of different membrane morphologies [Ref. 133]
The second class, the asymmetric membranes can be subdivided into three groups

(a) porous membranes; here the membranes do not have the same pore size over the whole membrane thickness but a pore size gradient;

(b) porous membranes having a top layer; these membranes have normally a top and open porous support layer, a second layer with much smaller pores (5-500 nm). Membranes of this type, called integrally skinned, are generally used in ultra filtration applications. In gas separation applications, the porous toplayer separate gases by Knudsen diffusion or Poiseuille mechanism. Alternately, the top layer may be dense and continuous polymer phase and only fluids hardly penetrate through the film.

(c) Composite membranes; a homogeneous layer is placed in a second production step on top of a support membrane.

The membranes used in pervaporation processes are classified according to the nature of the separation being performed. Hydrophilic membranes are used to remove water from organic solutions. These types of membranes are typically made of polymers with $T_g$ above room temperatures. PVA is an example of a hydrophilic membrane material. Organophilic membranes are used to recover organics from solutions. These membranes are typically made up of elastomers with $T_g$ below room temperature. The flexible nature of these polymers makes them ideal for allowing organic liquids to pass through. Examples include NBR, PB and SBR.

1.6. Liquid separation by pervaporation

Membranes can be used effectively to separate liquid mixtures in competition with traditional chemical processes such as distillation,
absorption, liquid extraction and fractional crystallisation. Pervaporation is an emerging membrane separation technique widely used today for the separation of organic liquid mixtures. This method attracted the attention of specialists in chemical and related fields like biochemical and petrochemical industries as an energy saving and environmentally friendly technology. One of the important features of this method is that it can be used to separate any liquid mixture in all concentration ranges [134,135].

The term “Pervaporation” indicates “Permeation” and “Evaporation” (Coined by P.A. Kober in 1917). Pervaporation is the selective evaporation of a component from a liquid mixture through a membrane. Pervaporation differs from other membrane separation methods in the fact that the material transported through the membrane undergoes a phase change. In pervaporation process, a thin polymer film is brought into contact with the liquid mixture (feed) and the penetrant dissolves and permeates through the membrane by a diffusion mechanism, along a concentration gradient. The permeate vapour can be condensed and collected or released as desired. The chemical potential gradient across the membrane serves as the driving force for the process. The driving force can be created by applying a vacuum on the permeate side to maintain the permeate vapour pressure lower than the partial pressure of the feed liquid. Figure 1.9 shows an overview of the pervaporation process [136].

![Figure 1.9: Overview of the pervaporation process (Ref. 136)](image-url)
1.6.1. Characteristics of the Pervaporation process include;

- Low energy consumption, minimum energy utilised is the enthalpy of vaporisation
- No entrainer required, no contamination
- Permeate must be volatile at operating conditions
- Functions independent of vapour/liquid equilibrium

1.6.2. Principles of pervaporation

In pervaporation, the liquid mixture is in direct contact with one side of the membrane and the permeated product is removed as vapour at the downstream side by applying a low pressure. The material transported undergoes a phase change. The minimum energy utilized is the enthalpy of vaporization of the permeate. The permeate composition is mainly determined by the relative affinities of the components in the feed to the membrane and their unequal mobilities through the membrane. Therefore, permeate composition will differ from that of feed composition. There are two approaches to describe the mass transport in pervaporation (1) the solution-diffusion model and (2) the pore flow model. The solution diffusion model is accepted by several researchers [137-139]. According to this mechanism, pervaporation consists of three consecutive steps (i) sorption of the permeant from the feed liquid to the membrane (ii) diffusion of the permeant in the membrane and (iii) desorption of the permeant to the vapour phase on the downstream side of the membrane (Figure 1.10) [139].
In general, the solubility and diffusivity are concentration dependent. Okada and co-workers [140-142] have proposed a transport model applicable to pervaporation on the basis of the pore flow mechanism. It is assumed that there are bundles of straight cylindrical pores on the membrane surface. The mass transport by the pore flow mechanism consists of three steps.

(a) Liquid transport from the pore inlet to a liquid-vapour phase boundary.

(b) Evaporation at the phase boundary and

(c) Vapour transport from the boundary to the pore outlet (Figure 1.11) [142]
The distinguishing feature of the pore flow model is that it assumes a liquid-vapour phase boundary inside the membrane and pervaporation is considered to be a combination of liquid transport and vapour transport in series. At present, it would be recognized that the two models represent two different approaches to the description of pervaporation transport.

### 1.6.3. Advantages of pervaporation process

Compared to the other competing technologies, pervaporation have the following benefits.

(i) Pervaporation is environmentally clean and energy efficient technology.

(ii) Simple equipment design and hence, involves low capital investment.

(iii) Process is completely enclosed, thereby minimising direct and fugitive emissions.

(iv) System is compact, modular and easily transportable.

(v) Low operating cost, and easy to scale up for industrial use.

**Figure 1.11:** Pore-flow model [Ref.142].
(vi) Reduces the energy demand because only the fraction of the liquid needs to be vaporized.

(vii) Opportunity for recovering concentrated organics.

1.6.4. Disadvantages of pervaporation process

Besides the advantages, pervaporation process also possesses several disadvantages. These include;

(i) Inadequate membrane material.

(ii) Fouling of the membrane.

(iii) Competition with established processes which are seen as safe options.

1.6.5. Major industrial applications.

Pervaporation offers significant capital and energy savings in applications that are difficult to separate by conventional techniques such as azeotropic mixtures or mixtures of close boiling components. The important industrial applications of pervaporation include [143].

(i) The treatment of waste water contaminated with organics.

(ii) Pollution control application.

(iii) Recovery of valuable organic compounds from process side streams.

(iv) Separation of 99.5% pure ethanol-water solutions.

1.6.6. Review on pervaporation

Separation of azeotropic, close boiling, isomeric or heat-sensitive liquid mixtures by membrane-based pervaporation technique has been studied extensively because of the potential industrial utility of this approach. Pervaporation is considered to be a promising alternative to conventional energy intensive technologies like extractive or azeotropic
distillation in liquid mixtures separation for being economical, safe and eco-friendly. Pervaporation has found viable applications [144] in the following three areas; (i) dehydration of organic solvents (e.g., alcohols, ethers, esters, acids); (ii) removal of dilute organic compounds from aqueous streams (e.g., removal of volatile organic compounds, recovery of aroma, and biofuels from fermentation broth); (iii) organic-organic mixtures separation (e.g., methyl tet-butyl ether (MTBE)/methanol, dimethyl carbonate (DMC)/methanol). Separation of organic-organic mixtures represents the most challenging application of pervaporation [145]. Most liquid pairs in this category are of industrial importance [146], such as polar/non-polar, e.g., methanol/MTBE [147-153], aromatic/aliphatic, e.g., benzene-n-hexane [154,155], aromatic/alcyclic, e.g., benzene/cyclohexane [156,157], and isomers, e.g., p-xylene, m-xylene, and o-xylene [158,159].

1.6.6.1. Organic solvent dehydration

Dehydration of organic solvents (e.g., alcohols, ethers, esters, acids, and ketones) largely represents the applications of the pervaporation [160-179]. The materials used in earlier dehydration research were the naturally occurring polymers, e.g., cellulose and cellulose derivatives [180]. Synthetic polymers e.g., poly (acrylic acid) (PAA), PVA, PAN, and nylon 6 were subsequently investigated, with a focus mainly on ethanol dehydration [181-183]. Many other hydrophilic materials were studied later and include sodium alginate, chitosan, polyethyleneimine (PEI), cellulose sulphate (CS). Uragami and Saito [184] and Mochizuki et al. [185] tried sodium alginate membranes for alcohol dehydration. Sodium alginate is a polysaccharide obtained from seaweeds, and it shows excellent affinity for water. However, as a membrane material, it lacks mechanical strength and stability in aqueous solutions. Yeom and co-workers [186,187] improved the membrane stability by crosslinking using glutaraldehyde. Huang et al. [188] also obtained stabilised sodium alginate membranes by using the method of
ionic crosslinking, which results from the interaction between the multivalent metal ions (e.g., Ca$^{2+}$, Al$^{3+}$) and the carboxyl group of the polymer.

Blending is also an effective approach for modifying the membrane properties. It was found that blending of alginate with other polymers could increase both the mechanical strength and stability of the membrane in aqueous solutions. Yang et al. [189] blended alginate with cellulose, and further crosslinked the alginate using Ca$^{2+}$. It was found that the tensile strength of the membrane was enhanced 12 folds and more importantly, the good separating performance of alginate was retained.

Ethanol dehydration using chitosan membranes was tried later and the continued research [190-195] indicated that chitosan is a very promising material for solvent dehydration and it demonstrated better separating performance than the crosslinked PVA. Dehydration of isopropanol and ethylene glycol using chitosan membranes was subsequently investigated by Feng and Huang [196]. Like sodium alginate, the chitosan membrane is extremely hydrophilic, and can lose membrane integrity in aqueous solutions. Crosslinking and blending techniques were employed to suppress the excessive membrane swelling and achieve the enhanced membrane stability. Crosslinked and blended chitosan membranes exhibit lower permeation flux, and higher selectivity [197-203]. Zareshki et al. [204] studied the pervaporation properties of poly lactic acid (PLA), a natural source polymer. PLA/PVP (poly vinyl pyrrolidone) blend membranes were evaluated in ethanol/ethyl tert-butyl ether azeotropic separation.

Yuan et al. [205] reported the dehydration of ethyl acetate aqueous solution by pervaporation using PVA/PAN hollow fiber composite membranes prepared by dip-coating method. The effects of crosslinking agents on the swelling degree and pervaporation performance of PVA/PAN membranes were investigated. The separation factor of the membrane increased while the permeation flux decreased with increasing content of
crosslinking agents. The pervaporation performance of PVA/PAN composite membrane for ethyl acetate/water solution was studied with respect to the feed temperature and feed water concentrations. Lin et al. [206] studied the dehydration of caprolactum by pervaporation using a PVA/ nano silica composite membrane. Roy et al. [207] used small flat dense samples of perfluorodimethylidioxole-tetrafluoro ethylene (PDD-TFE) copolymer membranes to separate water from hydrogen peroxide present in aqueous feed solutions.

1.6.6.2. Removal of dilute organics from water

The major contaminants in industrial waste water (i.e., petroleum refineries and chemical plants) and ground water are volatile organic compounds (VOCs), particularly chlorinated and aromatic hydrocarbons such as benzene, toluene, ethyl benzene and xylene. Conventional separation technologies such as distillation and liquid-liquid extraction are not applicable due to the large volumes of the waste streams required [208]. Currently employed methods for VOC removal are carbon absorption and air stripping. These methods are economical only at low VOC concentration such as below 100 ppm, and limited to non polar and volatile VOCs, respectively [209]. The need for frequent regenerations makes carbon adsorption economically unattractive for high VOC concentration streams. Post-treatments are required for air stripping to prevent a water pollution problem to become an air-pollution problem.

Pervaporation has emerged as a viable method for removing VOCs and other organic liquid mixtures such as azeotropic or close-boiling point mixtures from wastewater to yield a VOC concentrate which can either be destroyed by conventional means, such as incineration or be recycled for reuse [210]. The main problem in commercializing pervaporation for wastewater treatment is the high cost of the process. Several applications of pervaporation to VOC-laden wastewater have been reported in the literature.
Polydimethyl siloxane (PDMS) membranes have been studied as VOC permselective membranes, because they have high permselectivity and permeability for organic chemicals in water [214-216]. The high VOCs-permselectivity of the PDMS membrane is attributed to its stronger affinity for VOCs than for water. Another advantage of the PDMS membrane is high diffusivity of VOCs in the membrane due to its low Tg. Typical membrane materials used for organic removal from water and their performance is given in Table 1.5.

**Table 1.5:** Typical membrane materials for organic removal from water and their performance [Ref. 217-220]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Organics</th>
<th>Selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>Chloroform</td>
<td>6,800</td>
<td>217</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>25,000</td>
<td>218</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>11,000</td>
<td>219</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Toluene</td>
<td>10,000</td>
<td>218</td>
</tr>
<tr>
<td>Poly(ether-block-amide)</td>
<td>Trichloroethane</td>
<td>2,600</td>
<td>218</td>
</tr>
<tr>
<td>Nitrile rubber</td>
<td>Chloroform</td>
<td>18,000</td>
<td>219</td>
</tr>
<tr>
<td>Styrene-butadiene rubber</td>
<td>Chloroform</td>
<td>17,000</td>
<td>220</td>
</tr>
</tbody>
</table>

Recently, large number of reports on removal of volatile components from water is available in the literature [221-224]. Smuleac et al. [225] prepared a new type of pervaporation membrane (amorphous perfluorinated polymer, hydrophobic) and was studied for the separation of water–solvent mixtures. This membrane has high free volume and is inert for all solvents, and has a remarkable mechanical, chemical and thermal stability. The water is transported by solution diffusion model and the separation of solvent is primarily based on molecular sieving (size exclusion) principles. The
membrane showed a high stability for operation over a broad range of feed concentrations without swelling.

Chovau et al. [226] investigated the influence of downstream pressure on the pervaporative removal of toluene from water. An unfilled and filled PDMS membranes were compared with novel dense and porous SBS membranes. Experiments were performed by varying the downstream pressure from 1 to 40 mbar. The effect of filler incorporation into the polymeric network of PDMS-based membranes was also studied. It was found that the performance factors of all examined membranes were dependent on downstream pressure. Both the water and toluene flux decreased with increasing downstream pressure, the former being more pronounced, resulting in increased membrane separation factors. From the analysis of the intrinsic membrane properties it was found that toluene sorption was enhanced at higher downstream pressures. This resulted in membrane swelling, and hence higher water permeability than expected; nevertheless increased the membrane selectivity. Incorporation of the fillers into the PDMS network enhanced toluene removal rate and separation performance as well as intrinsic membrane properties. For the porous SBS membrane the highest toluene flux and permeability was obtained, but the lowest separation efficiency. The dense SBS membrane showed similar separation factors as the PDMS-based membranes, although a significantly higher toluene removal rate was observed.

Aliabadi et al. [227] investigated the use of polydimethylsiloxane (PDMS) composite membranes to study the removal of styrene from dilute aqueous streams by pervaporation. The influences of styrene feed concentration, permeate pressure, operating temperature, feed flow rate and membrane thickness on the pervaporation performance were investigated. The results showed that with the increase in concentration of styrene in the feed solution, both the permeation flux and the styrene
enrichment factor increase. Additionally, with a decrease in thickness of the membrane, the permeation flux was observed to enhance but the enrichment factor decreased. It was also indicated that increasing in the permeate pressure, reduces driving force for mass transfer and consequently the pervaporation performance dropped. The activation energy for pervaporation of both styrene and water calculated from Arrhenius plot indicated that the permeation of water through the membrane is higher temperature dependant than styrene.

1.6.6.3. Separation of organic-organic mixtures

The organic-organic separation attracted lots of research interest because of the huge industrial needs of efficient methods for separating mixtures like benzene/cyclohexane, benzene/hexane, toluene/heptanes, ethylbenzene/ xylene, p-xylene/o-xylene, etc. The components in these pairs have similar physicochemical properties, and effective separations of these mixtures are very difficult. Aptel et al. [228] applied pervaporation to separate organic liquid mixtures using a PTFE film grafted with N-vinylpyrrollidone for separating polar/non-polar mixtures like methanol/ toluene and obtained good selectivity but poor fluxes. Park et al. [229,230] investigated pervaporation separation of toluene/methanol and toluene/ethanol mixtures using blend membranes of poly (acrylic acid) (PAA) and PVA and found that membranes were alcohol selective. Flux decreased with increasing PVA content of the blend, but selectivity increased. Table 1.6 shows some typical membranes used for the separation of polar/non-polar solvent mixtures.
Table 1.6. Separation of polar/non-polar solvent mixtures (Ref. 231-238)

<table>
<thead>
<tr>
<th>No.</th>
<th>System (binary liquid mixture)</th>
<th>Membrane material</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Toluene/methanol</td>
<td>Poly(ethylene terephthalate)-graft-polystyrene</td>
<td>231,232</td>
</tr>
<tr>
<td>2.</td>
<td>Toluene/methanol</td>
<td>Acrylonitrile based copolymer</td>
<td>233</td>
</tr>
<tr>
<td>3.</td>
<td>Toluene/ethanol</td>
<td>Mixed matrix membranes of chitosan</td>
<td>234</td>
</tr>
<tr>
<td>4.</td>
<td>Toluene/methanol</td>
<td>Chemically modified poly(vinyl alcohol)</td>
<td>235</td>
</tr>
<tr>
<td>5.</td>
<td>Methanol/MTBE</td>
<td>Cellulose acetate filled with metal oxide</td>
<td>236</td>
</tr>
<tr>
<td>6.</td>
<td>Methanol/dimethyl carbonate</td>
<td>Crosslinked poly(vinyl alcohol)</td>
<td>237</td>
</tr>
<tr>
<td>7.</td>
<td>Toluene/methanol</td>
<td>Polyurethane/poly(dimethyl siloxane) blend (PU/PDMS)</td>
<td>238</td>
</tr>
</tbody>
</table>

Separation of aromatic hydrocarbon from aliphatic hydrocarbons is very important target in the membrane separation process of organic-organic mixtures. Among them, benzene/cyclohexane mixture is a tough system because both have very close boiling points and approximately equal molecular volumes. Various membranes like poly (vinylidene fluoride) [239], polyphosphonates of varied compositions [240], copolymers of acrylonitriles [241] etc. have been tried for separation of benzene/ cyclohexane mixtures by pervaporation. Tanihara et al. [242,243] used the polyetherimide segmented copolymer, and polyimide-co-polyphenylenediamine membranes for separating benzene/cyclohexane, benzene/heptane and acetone/ cyclohexane mixtures. The achieved separation factor of benzene to
Introduction

cyclohexane varied from 9 to 27, and the permeation rate varied from 0.4 to 2.7 kg/m²h.

Neel et al. [244] and Cabasso et al. [240,245] attempted polymer blending for the separation of benzene/cyclohexane and other mixtures like methanol/hexane and styrene/ethyl benzene. The blended polymers exhibited superior separating performance to the single materials. The blended membranes showed very good balance between the permeation flux and the separation factor, while single polymers usually give either high permeation rate (e.g., polyphosphonates, PE, PP), but low separation factor, or fairly good separation factor, but very low productivity (e.g., cellulose acetate, poly (vinyl fluoride)) [240]. Cabasso et al. [240,245] blended cellulose acetate and polyphosphonates, and the achieved separation factors of benzene/cyclohexane ranged from 12 to 40, and the permeation rate varied from 800 to 1000 ml/m²h. An et al. studied the performance of a PVC/EVA membrane for the pervaporation separation of benzene/cyclohexane mixtures [246]. Peng et al. [247] prepared a novel PVA/carbon nanotube hybrid membrane for the pervaporation separation of benzene/cyclohexane mixtures. Table 1.7 shows some membranes used for benzene/cyclohexane separation and their performance.
Table 1.7. Membranes used for benzene/cyclohexane separation and their Performance (Ref. 248-256)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Benzene (wt. %)</th>
<th>Temp (°C)</th>
<th>Flux (g/m²h)</th>
<th>Selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (PP)</td>
<td>55</td>
<td>25</td>
<td>54400</td>
<td>1.3</td>
<td>248</td>
</tr>
<tr>
<td>Low density polyethylene (LDPE)</td>
<td>50</td>
<td>25</td>
<td>10800</td>
<td>1.6</td>
<td>249</td>
</tr>
<tr>
<td>Poly (vinylene fluoride) (PDDF)</td>
<td>53</td>
<td>60</td>
<td>1600</td>
<td>6.2</td>
<td>250</td>
</tr>
<tr>
<td>Cellulose acetate-polyphosphonates (CA/PPN)</td>
<td>50</td>
<td>78</td>
<td>13600</td>
<td>40</td>
<td>240</td>
</tr>
<tr>
<td>Biphenyltetracarboxylic dianhydride-polyethylene oxide (BP-PEO)</td>
<td>60</td>
<td>70</td>
<td>2100</td>
<td>9.1</td>
<td>243</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)-ethylene glycol dimethacrylate (PMMA/EGDM)</td>
<td>10</td>
<td>40</td>
<td>8700</td>
<td>6.7</td>
<td>251</td>
</tr>
<tr>
<td>Nylon 6-g-polybutyl methacrylate</td>
<td>50</td>
<td>50</td>
<td>1120</td>
<td>2.2</td>
<td>252</td>
</tr>
<tr>
<td>Nafion-Ag⁺ (Sulphonated poly(perfluorinated ethylene)</td>
<td>50</td>
<td>50</td>
<td>2</td>
<td>12.7</td>
<td>253</td>
</tr>
<tr>
<td>Nafion-Cu²⁺ (Sulphonated poly(perfluorinated ethylene)</td>
<td>50</td>
<td>30</td>
<td>0.8</td>
<td>3.4</td>
<td>254</td>
</tr>
<tr>
<td>Polyurethane (PU)</td>
<td>54</td>
<td>25</td>
<td>325</td>
<td>2.7</td>
<td>255</td>
</tr>
<tr>
<td>Poly(vinylacetate)-Poly(vinyl alcohol) (PVAc-PVA)</td>
<td>50</td>
<td>25</td>
<td>500</td>
<td>7.5</td>
<td>256</td>
</tr>
</tbody>
</table>
Garg et al. [257] reported the preparation of poly(dimethyl siloxane) (PDMS)/clay nanocomposite membranes by in situ crosslinking of vinyl terminated PDMS (V-PDMS) resin in the presence of clay content varying from 1% w/w to 10% w/w in order to evaluate the influence of layered silicate on pervaporation characteristics of PDMS. Two commercial clays, Cloisite 30B and Nanomer 1.30P functionalized with polar and nonpolar surfactants were chosen for this purpose and PDMS membranes were prepared in the absence/or presence of varying amounts of different clays. Two nanocomposite membranes having PDMS/nanoclay (10% w/w) were selected based on their mechanical properties and evaluated for their performance in separating azeotropic toluene/methanol mixture. Composite membranes showed higher selectivity as compared to neat PDMS and toluene was a preferred permeant. The total flux for composite membranes was lower as compared to PDMS membrane. They have also investigated [258] the pervaporation properties of membranes based on interpenetrating polymer network (IPN) of vinyl terminated poly(dimethyl siloxane) (PDMS) and aromatic polyimide (PI). The modified membranes were prepared using simultaneous IPN (SIPN) technique by variation of polyimide loading of 5, 10 and 15 wt% respectively. IPN membranes prepared were employed in pervaporation separation of azeotrope forming toluene/methanol mixtures. The pervaporation properties could be tuned by adjusting the blend composition. All the blend membranes tested showed a decrease in flux with increasing polyimide content for methanol/toluene liquid mixtures. Toluene permeated preferentially through all tested blend membranes, and the selectivity increased with increasing polyimide content. The pervaporation characteristics of the blend membranes were also strongly influenced by the feed mixture composition. The flux increased exponentially with increasing toluene concentration in the feed mixtures, whereas the selectivities decreased for liquid mixtures.
A series of aromatic polyimides and polybenzoxazoles was synthesized and tested as membrane materials for separation of aromatic/aliphatic mixtures by pervaporation by Rebêiro et al. [259]. Homono- and random copolyimides were synthesized by a two-step polycondensation of a total of 6 diamines and 4 dianhydrides. Pervaporation experiments were conducted at 80°C with toluene/\(n\)-heptane or benzene/\(n\)-heptane mixtures as feed streams. All polymers were selective towards the aromatic hydrocarbon, whose permeability could be changed by approximately 4 orders of magnitude depending on the chemical structure of the diamine. Pure-liquid sorption experiments at 25°C revealed that these large changes in hydrocarbon permeability were mainly caused by changes in the diffusion coefficient.

1.7. **Vapour permeation**

Vapour permeation is one of the most prospective routes used in industries related to membrane technology. It employs a polymeric membrane as a semi-permeable barrier between a feed side under high pressure and a permeate side under low pressure [260]. Unlike pervaporation, the feed is a vapour and not a liquid, so there is no phase change or significant temperature difference across the membrane. Separation is achieved by the different degrees to which components are dissolved in and diffuse through the polymer. The polymers used in the membrane will hence depend on the types of compounds being separated [261]. The driving force can be approximated to the difference in partial pressures of the components in the feed. Compared to pervaporation, vapour permeation effectively increases the permselectivity of water and is capable of higher fluxes. The membrane area required is less and there is a lower likelihood of membrane damage by impurities in the feed [262]. In addition, the vapour permeation method promises greater simplicity in technical design and significant opportunities for energy savings [263]. It is
widely employed to separate azeotropes and in the dehydration of solvents/alcohols.

Vapour permeation, like pervaporation, works according to a solution-diffusion mechanism. The molecular interaction between the membrane and the separated species is the determining factor rather than the molecular size. The main component of the process is the membrane material which determines the permeation and selectivity and hence the separation properties of the process. The driving force for the mass transfer of permeate from the feed side to the permeate side of the membrane is the chemical potential gradient established by applying a difference in the partial pressures of permeate across the membrane [264].

The study of solvent vapour permeation offers a direct practical conclusion for the understanding and rational designs of volatile organic components (VOC) vapour recovery from a contaminated air stream. The method also promises significant opportunities for energy saving and solvent reuse compared with classical VOC control processes such as incineration, oxidation, and active carbon absorption. For VOC vapours recovery, as well as organic extraction from aqueous streams, a membrane material showing high organic vapour permeabilities but low air and water permeabilities is required in order to set up a competitive process [265].

Many research programmes focus on the development and optimization of novel polymeric membranes and their interaction with different penetrants to make vapour permeation more acceptable compared to other separation processes [266]. In this context, polymer blending is of great interest since it is an attractive and cost effective way for making materials with modulated properties for vapour permeation [267,268]. Conversely, the vapour permeation technique is a good tool for the thermodynamic characterization of polymer blends. The analysis of the
equilibrium sorption of a vapour by a blend can provide information on polymer-polymer interactions and morphology of the system [269].

The vapour permeation studies through different polymeric membranes have been reported by several researchers [270-274]. Yoshikawa et al. [275] conducted vapour permeation experiments with aqueous 2-propanol solution through gelatin/torlon poly (amide imide) blended membranes. The membranes were found to permeate water preferentially from the solutions. It has been proposed that membranes containing gelatine could be used as one of the promising materials for the dehydration of aqueous 2-propanol. Marais et al. [276] investigated the transport features of water vapour and gases (oxygen and carbon dioxide) through EVA films, and their blends with PVC. A plasticization effect of water was observed for EVA films with more than 19 wt. % of vinyl acetate (VA) content and for the EVA/PVC blends. For gas permeation, all the experimental sorption curves were found to be characterized by a constant diffusion coefficient, irrespective of the VA content of the copolymer used. The impressive use of NR and NR-based blends as membranes have inspired scientists to conduct various vapour permeation experiments using them [277]. The excellent oil resistant property of the NBR has been exploited in a large number of industrial applications [278,279].

Potreck et al. [280] investigated the transport behavior of a hydrophilic, highly permeable type of poly ethylene oxide (PEO)-based block copolymer as membrane material for the removal of water vapor from nitrogen using a multiple component feed mixture (water vapour and nitrogen). As determined from measurements with binary gas mixtures, the water vapor permeability increases exponentially with increasing water vapor activity whereas the nitrogen permeability slightly decreases with increasing water vapor activity. Consequently, the water over nitrogen selectivity increases with increasing water vapor activity. Friess et al. [281]
conducted a comparative study of the mass transport of two volatile organic compounds (VOCs), heptane and toluene and their binary mixtures through dense semicrystalline LDPE membranes at 25°C. The use of the widest possible concentration range and a set of different experimental techniques enabled to reveal differences between permeation and sorption of studied vapours and to clarify the effects of feed and instantaneous VPCs concentration inside the LDPE membrane.

Lue and co-workers have extensively conducted vapor permeation studies in poly (dimethyl siloxane) [282-286]. Lue et al. [286] examined the simultaneous removal and recovery of volatile organic compounds (VOCs) from permanent gaseous streams using vapor permeation (VP) technique. The VOC fluxes in multi-component feed systems were predicted using a PDMS membrane in the VP process. The investigated vapors included methanol, toluene, m-xylene, iso-pentane, and water. The solution-diffusion model derived from Fick's first law was used in establishing the mathematical models to describe the vapor permeation flux as a function of the downstream pressure and vapor activity level. The results demonstrated that the estimated vapor permeation fluxes were in good agreement with the experimental data.

Zhen et al. [287] prepared a PDMS–PVDF composite membrane using asymmetric PVDF hollow-fiber membranes as the substrate where a very thin layer of silicone-based coating material was deposited via a developed dip coating method. The preparations of the composite membranes under various conditions were investigated. The developed PDMS–PVDF composite membranes were applied for separation of a wide variety of volatile organic compounds (benzene, chloroform, acetone, ethyl acetate, and toluene). The results showed that the PDMS–PVDF hollow-fiber composite membranes that had been developed exhibited very high
removal efficiency (>96%) for all the VOCs examined under favorable operating conditions.

Yeom et al. [288] investigated the permeation performances of volatile organic compounds (VOCs)/nitrogen mixtures through PDMS. In the study, a series of chlorinated hydrocarbons, that is, methylene chloride, chloroform, 1,2-dichloroethane and 1,1,2-trichloroethane were adopted as organic vapor. The permeability, diffusion, and solubility coefficients of the VOC mixtures were evaluated from the determined permeation transients. The permeation performance of the mixture as well as the selectivity towards VOC component showed a strong dependence of both VOC content in feed and the condensability of VOC. In the permeation of the VOC mixture, the nitrogen permeability was depressed below pure nitrogen permeability by the preferential sorption of VOC into PDMS membrane. This effect was more noticeable for the more condensable VOCs. Also, it is observed that the permeation and separation of the mixtures were more controlled by sorption process rather than by diffusion process. Recently Jansen et al. [289] reported the gas and vapour transport through four different high fractional free volume amorphous glassy perfluoropolymers.

Sato et al. [290] investigated the diffusivity, solubility, and permeability of water vapor and nitrogen for Vacuum Ultraviolet (VUV)-irradiated poly (lactic acid) (PLA) membranes. The water vapor permeability of VUV-irradiated PLA membrane for 60 min was equal to that of unirradiated PLA membranes because the water vapor diffusivity reduction for surface crystallization counteracted the solubility enlargement for surface hydrophilicity. The temperature dependence on water vapor permeability of VUV-irradiated PLA membrane at low relative feed pressure showed that diffusivity-controlled behavior and that, at high relative feed pressure, diffusivity- and solubility-controlled behavior. Feng et al. [291] reported the removal of volatile organic compound (chloroform) from water by membrane
gas stripping using electro-spun poly(vinylidene fluoride) (PVDF) nanofiber membrane.

As with polymeric materials, fundamental technological properties are affected by polymer microstructure, the identification and subsequent assessment of structural transformations associated with the presence of solvent in the polymer network are of substantial interest, not least when long-term structural stability is concerned. Solvent-mediated morphological rearrangements are studied by Jeck et al. [292] on the basis of water vapour sorption into physically crosslinked PVA membranes. In a series of dynamic vapour-phase sorption experiments under well-defined boundary conditions, the semicrystalline polymer structure, as characterised by means of its degree of crystallinity, is analysed, providing information about time-dependent morphological behaviour as well as the spatial distribution of crystallinity across film thickness. Structural information thus obtained is then interpreted in view of the corresponding water uptake of the polymer network. Morphological rearrangements in the presence of solvent seem thus to be governed by two opposing effects. Upon water uptake, stretching of polymer chains may, on the one hand, induce part of the crystalline entities to unfold; at the same time, however, macromolecules equally gain mobility and may hence reorganise into more favourable ordered arrays. When compared to the swift disintegration of crystalline structures proceeding without any appreciable time lag to water diffusion into the film, the solvent-mediated organisation of mobilised polymer chains into three-dimensional ordered arrays involves more protracted realignments. The extent of molecular rearrangements affecting the structural stability of the polymer network could finally be shown to diminish upon repeated sorption and desorption.
1.8. Gas permeation

Gas permeation is another application of the rapidly growing membrane technology. Membrane based gas separation processes, over the last three decades, have proved their potential as better alternatives to traditional separation processes. The conventional processes, for example absorption, cryogenic distillation, and pressure swing adsorption (PSA) are energy intensive, as well as responsible for some environmental pollution. The membrane based separation processes are not only cost effective and environmentally friendly, but also, with many novel polymeric materials available, offer much more versatility and simplicity in customized system designs. Gas transport properties of polymer membranes are not only important to industrial production of high purity gases, but also plays a role in the application of membranes as barrier materials for food packaging and beverage industry. Because of many practical benefits, much effort is being exerted to understand the phenomena involved during gas transport through membranes as well as to synthesize novel polymers with better separation properties.

Traditionally the behaviour of gas transport through a gas separation membrane was presumably dominated by the diffusion of absorbed molecules. The gas flux was driven by the concentration gradient of absorbed molecules in polymer matrix. This leads to a simple model which is known as the solution diffusion model [293-295]. The permeating species interact with the polymer matrix and selectively dissolves in it, resulting in diffusive mass transport along a chemical potential gradient. Besides solution diffusion model, there are viscous flow, Knudson flow and molecular sieving for explaining gas transport through porous membranes. As illustrated in Figure 1.12, the mechanism of flow of gas molecules depends upon the size of the pores in relation to the mean free-path of the gas molecules [296]. In viscous flow, flow is inversely proportional to the viscosity of the fluid (gas). In contrast, flow is inversely proportional to the
square root of the molecular mass of diffusing species in Knudson flow. Ultra micro porous molecular sieving membrane has higher productivities and selectivities than solution diffusion mechanics [297, 298].

![Diagram of gas molecule flow](image)

**Figure 1.12:** Mechanism of flow of gas molecules (a) viscous flow (b) Knudson flow (c) molecular sieving and (d) solution-diffusion [Ref. 296].

The gas sorption through a homogenous polymer has been classified into two categories. For sorption to a rubbery polymer membrane, the sorption behaviour was described by Henry’s law. For sorption to a glassy polymer membrane, the sorption isotherm has been characterised by many authors by a dual sorption model. This combines two isotherms, a Henry-type isotherm for matrix absorption and a Langmuir-type isotherm for site sorption [299-303] (Figure 1.13) [304]. The gas transport behaviour for glassy polymer is then described by a so-called dual mobility model, which assigns two different diffusivities to the molecules absorbed by different mechanisms, Langmuir and Henry’s sorption. This model well described the pressure dependency of gas permeability of a wide range of glassy polymer membrane [305] and reasonably related the gas solubility to its permeability.
The difference in the transport and solution behaviour of gases in rubbery and glassy polymers is due to the fact that, the latter is not in a state of true thermodynamic equilibrium [119,305]. Rubbery polymers have very short relaxation times and respond very rapidly to stress that tend to change their physical conditions. Thus a change in temperature causes an immediate adjustment to a new equilibrium state. A similar adjustment occurs when small penetrant molecules are absorbed by a rubbery polymer at constant temperature and pressure and adsorption equilibrium is very rapidly established. In contrast, glassy polymers have very long relaxation times. Hence, in the presence of a penetrant, the motions of whole polymer chains or of portions thereof are not sufficiently rapid to completely homogenize the penetrant's environment. Penetrant (gas molecules) can thus potentially sit in holes or irregular cavities with very different intrinsic diffusional mobilities.

Gas separation by permeation through membranes has been suggested for many years [306-309]. For the efficient separation of gas
mixtures, the membranes should have a high selectivity for a particular gas over other gases. However, with homogenous membranes, high selectivity is usually associated with low permeability, as in the case of membranes used for enrichment of air [310]. On the other hand, porous membranes usually have very high permeabilities but their selectivity is generally low. The effect of incorporation of silica particles on the gas separation properties of EVA copolymer membranes has been investigated by Sadeghi et al. [311]. The EVA and hybrid EVA–silica membranes were prepared via thermal phase inversion method. Silica nanoparticles prepared by hydrolysis of tetraethylorthosilicate (TEOS), through the sol–gel mechanism. Gas permeation of EVA–silica nanocomposite membranes with silica contents of 5, 6 and 10 wt.% was studied for \( \text{N}_2 \), \( \text{O}_2 \), \( \text{CO}_2 \) and \( \text{CH}_4 \) single gases at pressures of 4, 6 and 8 bar. The obtained results suggest a significant increase in permeability of all gases and an increase in \( \text{CO}_2/\text{N}_2 \) and \( \text{CO}_2/\text{CH}_4 \) gases selectivities upon increasing the silica content. The increase in the gas permeabilities occurred due to increasing of the diffusivity and solubility of the gases in hybrid membranes. The permeability of condensable \( \text{CO}_2 \) and \( \text{CH}_4 \) gases increased more than noncondensable \( \text{O}_2 \) and \( \text{N}_2 \) gases due to their higher solubility in the membrane.

Zhang et al. [312] studied the gas permeation properties of natural rubber/kaolin composites. They have prepared a series of highly filled NR composites based on silane modified kaolin (SMK), precipitated silica (PS) and their mixed-compound additions (SMK+PS) by melt blending. Compared to the pure NR, these highly filled NR/SMK composites exhibited outstanding mechanical properties and excellent gas barrier properties (Figure 1.14).
The gas barrier properties of NR composites with SMK and PS were much higher than those of NR/PS composites and better than those of NR/SMK. The nitrogen permeability of NR/SMK composites was decreased by 20-40% after filling with kaolin. The significant improvement in these properties is attributed to the parallel kaolinite particles which restricted the free movement of rubber chains and retarded the diffusion of the gas molecules. The highly filled composites can be used to improve the air-tightness of rubber products.

A variety of techniques have been used to measure gas permeation through polymer membranes. In essence, the object of a permeation experiment is to measure the rate of transport of penetrant through a film as a function of time. There are three basic methods of measuring penetrant transmission rates; pressure, volume and concentration change methods. These are depicted schematically in Figure 1.15 [1].

Barrer [313] first developed the high vacuum pressure change method and it was later refined by Stannet and co-workers [314] to determine the diffusion and permeability coefficients of gases and vapours. The film under test is placed in a stainless steel cell, which is divided into
two chambers. Both sides are evacuated, and the residual vapours frozen out with liquid nitrogen. The penetrant, which can be a gas, vapour or liquid, is admitted to one chamber, and the increasing pressure in the other is measured with a suitable gauge.

The volume change method was developed by Todd [315], which employed a cell having a large volume on one side and small volume on the other. The large chamber was evacuated and the test gas introduced into the small chamber at atmospheric pressure. A horizontal capillary connected to the small chamber contained a mercury plug. As gas permeated into the large chamber, the mercury plug moved in the capillary so as to reduce the volume of the small chamber and maintain the pressure. By observing the speed with which the plug moved, the rate of permeation could be determined.

Figure 1.15: Schematic diagram of permeation methods [Ref. 1]
The concentration change method avoids the necessity for a total pressure difference across the film, and relies on a difference in concentration or partial pressure of penetrant. Here also, the permeation cell is divided into two chambers by the film under test. The penetrant flows over one side of the film under test, either as a pure gas or as a vapour in a carrier gas stream, and is termed the ‘span’ gas stream. The permeating gas is swept away by a second carrier gas stream (the sweep gas stream), which is then analysed. Chemical methods or modern instrumental methods, capable of much greater sensitivity, have been used to determine the amount of permeating gas [316]. A novel permeation apparatus is developed which can make the on-line measurements of both flux transient and permeate composition in gas permeation. It is based on the continuous-flow technique employed previously for liquid permeation. The transient measurement allows the simultaneous determination of permeation characteristics, such as, permeability, diffusion and solubility coefficient, and activation energies with one experiment.

A serious drawback associated with permeation methods is the problem of leaks. These can occur at the edges of the film or through pinholes in the exposed area. The former can be avoided to some extent by sophisticated design (eg., mercury seals), but leaks remain a frequently undetected source of error and can only be assumed absent when the two lowest results are in good agreement.

Although the concept of separating gases with polymeric membranes was developed a long time ago, the widespread use of gas separation membranes has occurred only within the past 10 to 15 years. The primary reason for this was that the early membranes were insufficiently permselective and exhibited insufficient fluxes so that the cost of membrane processes never successfully competed with the cost of conventional processes. However, modifications in the physical and chemical structures
of membranes have enhanced separation characteristics. Now there are several important industrial applications (as indicated in Table 1.8. [296] where membrane operations can be competitive with more traditional methods of gas separations, such as cryogenic separation and pressure-swing adsorption (PSA). These include oxygen enrichment of air, hydrogen separation from carbon monoxide and other gases, removal of carbon dioxide from natural gas, and the reduction of organic vapour concentration in air. Other smaller-scale applications include the preservation of food such as apples and bananas during transport by blanketing with low-oxygen-content air, the generation of inert gases for safety purposes, and the dehydration of gases.

**Table 1.8:** Applications of polymeric membranes in gas [Ref. 296].

<table>
<thead>
<tr>
<th>Separation</th>
<th>Suitable Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen / Nitrogen</td>
<td>Silicone rubber</td>
</tr>
<tr>
<td></td>
<td>Polysiloxane-block-polycarbonate</td>
</tr>
<tr>
<td></td>
<td>Polysulfone</td>
</tr>
<tr>
<td></td>
<td>Ethyl cellulose</td>
</tr>
<tr>
<td></td>
<td>Poly [1-trimethylsilyl]-1-propyne</td>
</tr>
<tr>
<td></td>
<td>Polypyrrolone</td>
</tr>
<tr>
<td></td>
<td>Polytriazole</td>
</tr>
<tr>
<td></td>
<td>Polyaniline</td>
</tr>
<tr>
<td>Hydrogen from carbon monoxide, methane, nitrogen</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>Acid gases (CO$_2$ and H$_2$S) from hydrocarbons (eg., natural gas and enhanced oil recovery)</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td></td>
<td>Poly (vinyl chloride)</td>
</tr>
<tr>
<td></td>
<td>Polysulfone</td>
</tr>
<tr>
<td></td>
<td>Polyetherimide</td>
</tr>
<tr>
<td>Hydrocarbon vapours from air</td>
<td>Silicone rubber</td>
</tr>
</tbody>
</table>
A comprehensive review on gas separation with polymer membranes has been done by Maier [317]. Increasing industrial interest in the applications of permselective polymeric membranes has generated an abundance of research in the past 20 years [318-340]. Stephen et al. [341] investigated the gas permeability coefficient of nano and micro composites of NR, XSBR and 70:30 NR/XSBR blend membranes with special reference to type of filler, gases, filler loading and pressure. The layered silicates such as sodium bentonite and sodium fluorohectorite were the nanofillers used and the conventional microfillers were clay and silica. Micro filled samples showed higher permeability and this is ascribed to the poor physical interaction between the polymer and filler leading to aggregation of fillers. The size of the penetrant gas molecules affected the permeability coefficient. The covalent radii of nitrogen gas molecule are higher than oxygen gas molecule and hence nitrogen gas showed reduced permeability. It was also found that the gas barrier properties of nano filled latex membranes were very high.

Rutherford et al. [342] conducted the gas transport in EPDM elastomer. They have undertaken permeation measurements with EPDM in an effort to characterize the gas transport properties of this barrier material. The derived solubility and diffusivity of a series of probe gases including helium, hydrogen, neon, argon, krypton, oxygen, nitrogen, carbon dioxide and methane were compared with molecular simulation prediction. Agreement between the molecular simulations and experimental data is obtained for simple spherical monoatomic probe gases, with greater deviation observed for non-spherical polyatomic gases.

Kirkland and Paul [343] investigated the gas permeation response of poly(\(n\)-alkyl acrylate) and poly(\(m\)-alkyl acrylate) blends as a function of temperature for varying side-chain lengths and blend composition in the semi-crystalline and molten states. Permeation responses of the blends
investigated in some cases exhibited two distinct permeation jumps or increases at the melting temperature of each component. Blends with continuous permeation responses but higher effective activation energies of permeation (i.e., more thermally responsive) were observed for some blends over the temperature of interest for membranes to be used for modified atmosphere packaging.

Dobre et al. [344] reported the experimental and processed data of gas permeation through stretched NR membranes. As a consequence of the membrane stretching, the polymer chains flexibility decreases and the penetrant path length increases. Gas diffusion, solubility and permeability coefficients depend on stretching intensity. Two methods were used to estimate the permeability coefficients of pure gases, i.e. hydrogen, oxygen, nitrogen, methane and carbon dioxide. A dynamic method was based on volume and pressure measurements of rubber balloons filled with gas. A time-lag method was employed to study the gas permeation through rubber membranes placed in a permeation cell. Both methods gave comparable results.

Many industrial gas separations in which membrane processes are feasible entail high water vapour contents, as in CO\textsubscript{2}-separation from flue gas in carbon capture and storage, or in biogas/natural gas processing. Studying the effect of water vapour on gas permeability through polymeric membranes is essential for materials design and optimization of these membrane applications. In particular, for amine-based CO\textsubscript{2} selective facilitated transport membranes, water vapour is necessary for carrier-complex formation. Conventional polymeric membrane materials can vary their permeation behaviour due to water-induced swelling. Roman et al. [6] reported a simple approach to gas permeability measurement in the presence of water vapour, in the form of a modified constant volume/variable pressure method (pressure increase method).
Sadeghi et al. [345] investigated the effect of silica nanoparticles on the gas permeation properties of polyether-based PU membrane. Gas permeation properties of PU–silica nanocomposite membranes with silica content of 2.5, 5, 10 and 20 wt.% was studied for pure CO$_2$, CH$_4$, N$_2$ and O$_2$ gases. The obtained results indicated the reduction in permeability of all gases, but enhancement in CO$_2$/N$_2$, CO$_2$/CH$_4$ and O$_2$/N$_2$ selectivities was observed by increasing the content of non-permeable silica nanoparticles in PU–silica membranes. In the case of PU–silica (20 wt.%) nanocomposite membrane, the obtained CO$_2$/N$_2$ selectivity was 1.65 times of pure PU, while the CO$_2$ permeability reduction of PU–silica membranes was 35.6% in comparison with pure PU.

The gas permeation and transport characteristics of sour gases (CO$_2$, H$_2$S and SO$_2$) were investigated and analyzed by Ren et al. [346] using poly (amide-6-b-ethylene oxide) (PEBA1657) membranes. With the increase of transmembrane pressure difference, the permeation of H$_2$S, CO$_2$ and SO$_2$ is enhanced due to pressure-induced plasticization effect. This has been shown in Figure 1.16.

![Figure 1.16](image)

**Figure 1.16.** Influence of transmembrane pressure difference on the gas permeability of PEBA1657 copolymer at 25°C (Ref. 346).
1.9. Purpose and importance of the work

The development of new membranes and their utilization for the separation of liquids and gas mixtures is an important technique in membrane science and technology. Tremendous opportunities exist for this and the level of research and developmental activity in the field of membrane science and technology has been rising dramatically all over the world during the past two decades. This is happening not only because of the growing recognition of the commercial potentialities of membrane separation, but also because of the growing realization of the scientific and engineering community that synthetic membranes can play a significant role for society and industry.

Ethylene propylene diene monomer (EPDM) rubbers have proven to be useful barrier materials in the automotive, electrical and industrial construction industries due to their unique mechanical and chemical properties. EPDM exhibits excellent resistance to weather, ozone, acids and alkalies while accommodating high volume fractions of filler and liquid plasticisers and retaining desirable physical and mechanical properties [347]. Although this elastomer is primarily used in the automotive, electrical and industrial construction industries, new applications in commercial separation and purification industries are also being forged [348,349]. Despite its importance in sealing and separation applications, a fundamental understanding of transport phenomena through EPDM is still incomplete. Further investigation is required for estimating the solubility and diffusivity of liquids, vapours and gases in this elastomer. An understanding of transport studies through EPDM is useful for application to membrane based gas separation operations, for evaluating EPDM as a potential material for barrier and sealing applications and for predicting the extent of oxidative ageing when ageing reactions are fast in comparison to oxygen diffusion.
For the last few decades, the performance of the EPDM rubber has been tried for improvement in properties by blending with various polymers. HDPE has a unique set of properties including excellent mechanical properties, ozone resistance, good electrical properties and chemical resistance, but has poor stress crack resistance. Blends of HDPE and EPDM are a new class of thermoplastic elastomers, which couple the superior properties of HDPE and EPDM and open up new avenues for the commercial use of these blends [350-353]. High performance thermoplastic elastomers (TPEs) can be prepared by blending EPDM and HDPE. These blends exhibit the excellent processing characteristics of thermoplastics and the very good elastic properties of rubber. The blending of EPDM with HDPE was found to improve the physical and mechanical properties of EPDM [354,360]. Further, these blends are low cost materials, which find application in cables, footwear, films, automobile components, moulded articles such as electrical components, toys etc. Being TPEs, these blends can be recycled. These blends are expected to have good mechanical strength, good processability, good impact strength, good insulation properties and resistance to moisture and chemicals.

1.10. Objectives of the study

The main objectives of the present study are the following.

1.10.1. Effect of nature of crosslinks on the transport behavior of EPDM membranes

As a first step in developing new membranes based on EPDM, it was vulcanised by four different systems viz, Conventional (CV), Efficient (EV), Semi-efficient (SEV) and Sulphurless (S-less), which produced four types of crosslinks between the rubber chains. In the sulphurless system and EV system, mono and disulphidic linkages are present, conventional Vulcanized samples have mainly polysulphidic linkages in addition to pendant sulphides and cyclic polysulphides, and samples vulcanized using
SEV system have mono, di, and polysulphidic linkages. The nature as well as distribution of the crosslinks controls the overall properties. Hence, the effect of nature of crosslinks, penetrant size, temperature etc. on transport behavior of EPDM were analysed in detail.

1.10.2. Development of EPDM/HDPE blend membranes

EPDM/HDPE blend membranes were prepared by melt blending technique in a Brabender Plasticorder. The diffusion characteristics of the blends were studied in terms of the blend ratio, morphology, penetrant size, temperature, dynamic vulcanization etc. The mechanical properties of the blends were also examined. We have also looked into the relationship between dynamical mechanical behavior and transport characteristics of EPDM/HDPE blends.

The transport behavior of these blends using different organic liquids was examined. Two types of organic liquids viz. aromatic and aliphatic hydrocarbons which have closer solubility parameter values of the polymer have been selected for the investigation. The aromatic hydrocarbons used were benzene, toluene, p-xylene and mesitylene. The aliphatic hydrocarbons selected were normal alkanes viz. n-pentane, h-hexane, n-heptane and n-octane.

The experimental observations were used to estimate different kinetic parameters such as diffusion coefficient, sorption coefficient, permeability coefficient and thermodynamic parameters such as enthalpy, entropy, activation energy. The mode of transport was also examined. These parameters are highly useful for developing clear theoretical generalization regarding the nature of the polymers towards different liquids.

The solvent transport through rubber matrix is also strongly influenced by the presence of fillers. The degree of reinforcement varies with the type and dosage of fillers. The flexibility and free volume of the
network decrease considerably with increase in reinforcement. The filler reinforced materials exhibit high strength compared to gum vulcanizates, which is essential for the smooth functioning of the membranes. Hence it is relevant to examine the effects of particle size, shape and structure of the fillers on the transport process.

1.10.3. Pervaporation studies

The feasibility of utilising EPDM/HDPE blend membranes for the pervaporation separation of organic liquid mixtures has been examined. The influence of factors such as crystallinity, feed composition, nature of crosslinks, degree of crosslinking and penetrant size on the separation have been analysed in detail.

1.10.4. Vapour permeation studies

Analysis of equilibrium sorption of a vapour by the solid polymer blend can provide useful information regarding the polymer-polymer interactions. The amount of vapour sorbed is related to its interaction with the blend. Hence, the vapour permeation behaviour of EPDM and EPDM/HDPE blends were studied using chlorinated hydrocarbons such as dichloromethane, chloroform and carbon tetrachloride as the molecular probe. This behaviour was compared with the morphology of the blends.

1.10.5. Gas permeation studies

Development of membranes with high permeability and high permselectivity has become an active field of investigation because of an increased interest in the membrane process for gas separation. Therefore, the permeation characteristics of EPDM and EPDM/HDPE blend membranes were investigated with oxygen and nitrogen. The motive behind this study is to use these membranes for gas separations.

Finally attempts were made to compare the experimental results with theoretical predictions in appropriate cases.
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