CHAPTER 1

INTRODUCTION
Towards the end of twentieth century great attention has been focused on the field of diffusion, sorption and permeation because these basic phenomena play a vital role in several important areas of engineering and industry. These include protective coatings such as paints and varnishes, electronic devices and cable materials, packaging materials for foods and vegetables, biomedical devices, etc. The transport studies are of considerable importance when we come across problems like designing a barrier material or tubes for transporting liquids and gases.

Recently, a combination of improved economics and better technology has resulted in membrane products that signed a new era in the commercial use of membranes for liquid and gas separations. The advantages of membrane separation over conventional process consists of reduced capital cost, lower energy consumption, smaller size and light weight, lower installation costs due to its modular design and simplified operation. Membrane separation techniques have already been used in industrial applications like desalination of brine, salt manufacturing from sea-water and oxygen enriched air. Another technique of importance is pervaporation, which has been recently used for the separation of a wide variety of organic liquid mixtures. In order to design highly efficient and economically viable barrier materials and membranes, elucidation of the
relationship between transport properties and molecular structure of polymers is necessary.

The aim of research in this field is to establish mechanisms and laws relating solubility and transport in polymer membrane to their molecular properties, the nature of the penetrants and the film morphology. Therefore, small molecules are used as a molecular probe for investigating the link between transport phenomena and polymer structure.

1.1. Fundamentals of transport phenomena

The transport of small molecules through a polymer membrane occurs due to random molecular motion of individual molecules. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between two phases. The transport process slowly tries to equalise the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane. This process can be described in terms of Fick’s first law of diffusion according to which the flux $J$, in the direction of flow is proportional to the concentration gradient ($\frac{\partial c}{\partial x}$) as

$$ J = -D \left( \frac{\partial c}{\partial x} \right) $$

(1.1)

Here $D$ is the diffusion coefficient. Equation (1.1) is applicable to the diffusion in the steady state, i.e., when the concentration does not vary with time. On the other hand, Fick’s second law describes the nonsteady state for transport process, which is given by the rate of change of penetrant concentration ($\frac{\partial c}{\partial t}$) at a plane within the membrane

i.e.,

$$ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right) $$

(1.2)
This is the ideal case in which the membrane is isotropic and the diffusion coefficient is independent of distance, time and concentration. Depending on the boundary conditions many solutions are available for equation (1.2).

Strong polymer penetrant interaction occurs with many organic penetrant molecules and hence D is dependent on concentration. Therefore, equation (1.2) becomes,

$$\frac{\partial c}{\partial t} = D \frac{\partial D(c) (\partial c / \partial x)}{\partial x}$$  \hspace{1cm} (1.3)

Analytically this cannot be solved easily and hence another form of equation is commonly used.

$$\frac{\partial c}{\partial t} = D(c) \frac{\partial c^2}{\partial x^2} + \frac{\partial D(c)}{\partial c} \left( \frac{\partial c}{\partial x} \right)^2$$  \hspace{1cm} (1.4)

Generally experiments are conducted over relatively small intervals of c and the term \((\partial D(c)/\partial c)\) is negligible compared to \(D(c)\). Then we get a mean or integral diffusion coefficient \(\bar{D}\) over a concentration range \(c_1\) to \(c_2\) as given by

$$\bar{D} = \int_{c_1}^{c_2} D(c) \frac{dc}{c_1 - c_2}$$  \hspace{1cm} (1.5)

where \(c_1\) and \(c_2\) are the concentration of penetrant at the low and high concentration faces of the film, respectively.

In the steady state, diffusion flow is constant and the diffusion coefficient is independent of concentration. Then equation (1.1) may be integrated to give

$$J = \frac{D(c_1 - c_2)}{h}$$  \hspace{1cm} (1.6)

where \(h\) is the membrane thickness. The penetrant distribution between the penetrant and the polymer phase is described by the Nernst distribution law.

$$c = KC$$  \hspace{1cm} (1.7)
where \( c \) is the sorbed concentration; \( C \), the ambient penetrant concentration in contact with the polymer surface and \( K \) depends on temperature and \( c \). In the case of transport of gases and vapours, pressure \( p \) is used instead of surface concentration. According to Henry's law

\[
c = S_p
\]  

where \( S \) is the solubility coefficient. Combination of equations (1.6) and (1.8) gives the well-known permeation equation

\[
J = \frac{DS(p_1 - p_2)}{h}
\]  

where \( p_1 \) and \( p_2 \) are the ambient pressures on two sides of a film of thickness \( h \). The product \( DS \) is called the permeability coefficient \( P \), so that

\[
P = D.S
\]  

In terms of permeability, the flux equation (1.9) can be written as

\[
J = \frac{P(p_1 - p_2)}{h}
\]  

1.2. Factors contributing the transport process

1.2.1 Nature of the polymer

The transport behaviour for a given penetrant varies from one polymer to another. Transport properties depend on the free volume within the polymer and the segmental mobility of the polymer chains. The segmental mobility of the polymer chains is affected by the extent of unsaturation, degree of crosslinking, degree of crystallinity and nature of substituents. The glass transition temperature of polymers has a profound influence on transport properties. Polymers with low glass transition temperature, possess greater segmental mobility and will have higher diffusivity. This is clearly illustrated in Figure 1.1.
The considerable increase of $D_0$ with decreasing value of $T_g$ is accompanied by a considerable decrease in the concentration dependence of the diffusion coefficient. For an example, the diffusion coefficient of benzene in natural rubber, polyethylacrylate and polymethacrylate, with $T_g$ values of 200, 250 and 280 K respectively, increases by 2.9, 20 and 340 times on increasing the volume fraction of benzene from 0 to 0.1. Barrer et al.\textsuperscript{12} have shown that diffusion coefficient of krypton on silicone rubber at 25°C is $1.3 \times 10^{-9}$ m$^2$ s$^{-1}$ whereas in poly(vinyl acetate) at the same temperature it is $1.9 \times 10^{-13}$ m$^2$ s$^{-1}$. This effect can be correlated with a considerable drop in $T_g$.

It is found that diffusivity is decreased when unsaturation in polymer backbone is decreased by hydrogenation. Auerbach et al.\textsuperscript{13} 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 because unsaturation in polymer chains provides segmental mobility, whereas saturation restricts it.

Barrer and Skirrow\textsuperscript{14} have studied the diffusion of a series of alkanes through rubbers and reported that for low levels of crosslinking, the diffusivity decreased linearly with increase in crosslink density. At higher levels of crosslink density, the rate of decrease of diffusivity levelled off.

Introduction of bulky or polar substituents on the polymer chain influences the transport process. Van Amerongen\textsuperscript{15} has reported that rubbers containing large numbers of substituent methyl groups have lower diffusivity. For instance, the low permeability of butyl rubber is due to the sluggish segmental motion of the polymer chains caused by the steric hindrance of the two pendant methyl groups on every other main chain carbon atoms. Data shown in Table 1.1 demonstrate that for polymers with the same substitution pattern, it is flexibility of the backbone that dominates the permeation properties.\textsuperscript{16}

**Table 1.1.** The effect of side chain and main-chain substitution on oxygen permeability.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T\textsubscript{g}(°C)</th>
<th>p \times 10^{-17} (mol m^{-1}s^{-1} Pa^{-1})^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-CH\textsubscript{2}CMe\textsubscript{2}-</td>
<td>-76</td>
</tr>
<tr>
<td>B</td>
<td>-CH\textsubscript{2}SiMe\textsubscript{2}-</td>
<td>-92</td>
</tr>
<tr>
<td>C</td>
<td>-OSiMe\textsubscript{2}-</td>
<td>-123</td>
</tr>
<tr>
<td>D</td>
<td>Me Me</td>
<td>-88</td>
</tr>
<tr>
<td></td>
<td>(\text{Si(CH}_2)_8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{SiO}^{-})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Me Me</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Ph</td>
<td>-28</td>
</tr>
</tbody>
</table>

^aAt 35°C. [Source: Ref. 16].
The Si-O backbone allows rapid chain segment motion to occur in the silicone rubber (Polymer C) and substitution of the Si-O linkage by Si-CH₂ (Polymer B) dramatically reduces the permeability to a value even less than that of butyl rubber (Polymer A). Insertion of (CH₂)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 the increasing rigidity of the polymer backbone and the decreasing free volume available for the diffusion of permanent molecules. The substitution of bulky functional groups in the side chains appears to have a greater influence on decreasing the diffusivity than substitution of these groups in the polymer backbone.16-18 Generally, the diffusivities of small permeant molecules are reduced less relative to larger penetrant molecules, implying that the polymer matrix can act rather like a 'molecular sieve'.

It was also reported that polymer molecular weight significantly influences the transport process. As 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. For instance, for a series of polystyrene samples, the diffusivity of a range of organic vapours (acetone, benzene etc.) decreased by a factor of almost ten as molecular weight increased from 10000 to 300000.19

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 1.2.20
Table 1.2. Effect of Functional groups on oxygen permeability of Vinyl Polymers (CH₂CHX)ₙ

<table>
<thead>
<tr>
<th>Functional group</th>
<th>p x 10⁻¹⁷ (mol m⁻¹ S⁻¹ Pa⁻¹)*</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>3.97 x 10¹</td>
</tr>
<tr>
<td>F</td>
<td>3.96 x 10²</td>
</tr>
<tr>
<td>Cl</td>
<td>2.1 x 10²</td>
</tr>
<tr>
<td>CN</td>
<td>1.08 x 10⁴</td>
</tr>
<tr>
<td>OH</td>
<td>2.64 x 10⁵</td>
</tr>
</tbody>
</table>

*At 23°C, 0% relative humidity. [Source: Ref. 20].

1.2.2 Nature of crosslinks

For the same polymer at the same crosslink density, transport phenomena depend on the nature of the crosslinks. Poh et al.²¹ have studied sorption behaviour of bulk and solution crosslinked natural rubber networks prepared by irradiation with γ-rays. They found that in benzene solution crosslinked networks swell more than the corresponding bulk crosslinked networks having the same crosslink density.

1.2.3 Effect of plasticizers

The addition of plasticizers to a polymer results in increased segmental mobility and usually an increased penetrant transport. Detailed accounts on the effect of plasticizers and humidity have been given by Stannett et al.²² Barrer et al.²³ have reported the increase in diffusion coefficient for the transport of hydrogen and neon through poly(vinyl chloride) on adding tricresyl phosphate as
plasticizer to the polymer. But the plasticizer was found to lower the solubility coefficient.

1.2.4 Nature of the penetrant

The size and shape of penetrant molecule will influence its rate of transport within the polymer matrix. The decrease in diffusivity with increase in the size of the penetrant has been reported by many investigators.\textsuperscript{24,25} Kim \textit{et al.}\textsuperscript{26} have reported decrease in equilibrium penetrant uptake with increasing penetrant chain length in the transport of alkanes from heptane to dodecane through crosslinked polystyrene. Permeant shape has a noticeable effect on permeability. For instance, flattened or elongated molecules have higher diffusion coefficients than spherical molecules of equal molecular volume\textsuperscript{19,27} Generally, permeant size and shape effects are much more marked in glassy than in rubbery polymers. This arises from the differences in the permeant polymer mixing processes. In rubbery polymers, energy is required to generate sites for the permeant molecules to occupy but, since increasing permeant size tends to increase the heat of sorption, it follows that larger permeant molecules will be readily sorbed leading to enhanced plasticization of the polymer chains. Consequently, whilst smaller permeants will have a greater diffusion coefficient, the polymer will be less plasticized, whereas the lower diffusion coefficient of the larger permeants will be compensated for by the higher degree of sorption. The overall effect is to minimise the difference in the permeation coefficient for large and small permeants.

1.2.5 Fillers

The diffusion and transport in filled polymers depend upon the nature of fillers, degree of adhesion and its compatibility with polymer matrix. If the inert filler used is compatible with the polymer matrix, the filler will take up the free volume within the polymer matrix and create a tortuous path for the permeating
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, an increase in permeability. Coran et al. studied the transport of solvents in unidirectional rubber-fibre composites and concluded that fibres restrict the solvent uptake. Equilibrium swelling in solvents is 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 fibre rubber adhesion.

Das reported that restricted equilibrium swelling is a true measure of adhesion between short fibres and rubber. Varghese and co-workers used equilibrium swelling as a probe for investigating the adhesion between short sisal fibre and natural rubber. The restriction on elastomer swelling exerted by sisal fibre as well as the anisotropy of swelling of the composite have been confirmed. The swelling decreased with increase of fibre content and also with the addition of bonding agent. They have also found from swelling studies that chemically treated fibres have got better adhesion to natural rubber than untreated fibres.

1.2.6 Temperature

The variation of diffusivity, soptivity and permeability coefficients with temperature is described by the following Arrhenius relationship.

\[
D = D_0 \left( e^{-\frac{E_D}{RT}} \right) \tag{1.12}
\]

\[
S = S_0 \left( e^{-\frac{\Delta H_s}{RT}} \right) \tag{1.13}
\]

\[
P = P_0 \left( e^{-\frac{E_p}{RT}} \right) \tag{1.14}
\]

where \(E_D\) and \(E_p\) are the activation energies of diffusion and permeation respectively, \(\Delta H_s\) is the heat of solution of the penetrant in the polymer and \(D_0, S_0\) and \(P_0\) are the pre-exponential factors.
There are reports relating to the deviations from the above relations, especially in the region of glass transition temperature of the polymer concerned, where a break between two straight lines in the Arrhenius plot is often observed. The calculated activation energy values are normally greater above $T_g$ than below it. A typical example is the data of Mears$^{34}$ for the diffusion, solubility and permeation of hydrogen, helium, oxygen, neon and argon through poly(vinyl acetate).

1.3. Transport phenomena in different polymeric systems

1.3.1 Diffusion in rubbery polymers

The face indices of rubbery polymers are unsaturation, segmental mobility and the large amount of free volume between the molecules. Hence smooth and easy diffusion of small molecules through rubbery polymers is usually observed. Owing to its two phase-morphology, the transport of organic solvents through polyurethane (PU) membrane is highly interesting. Hung and Autian$^{35}$ studied the transport behaviour of PU in a series of aliphatic alcohols in the temperature range of 24-50°C by using thermogravimetric sorption method. The diffusivity values were calculated from the desorption curves by means of integrated form of Fick’s relation. The diffusion coefficient, $D$, was found to increase with temperature and decrease with increase in molecular weight of penetrants. On the other hand, the branched alcohols exhibited lower ‘$D$’ values as expected. The activation energies ($E_D$) for diffusion were also calculated. The $E_D$ values increase with increase in molecular size and the diffusion results were analysed on the basis of Eyring hole theory.$^{36}$

Later Hung$^{37}$ conducted TGA studies on the interactions of a wide range of organic liquids, having a variety of structural/functional groups with the polyurethane membrane. He examined the effect of temperature, molecular size, polarity of solvent etc. on the interactions. Among the solvents used chlorobenzene
exhibited a strong affinity for polyurethane. But hexane, the symmetrical nonpolar solvent showed less interaction with PU membrane. Diffusion coefficient was found to follow an inverse relationship with the size of the molecule.

Hopfenberg and co-workers\textsuperscript{38} have reported steady state permeation rates in equilibrium sorption for a series of alcohols (C\textsubscript{1}-C\textsubscript{7}) in a polybutylene adipate polyurethane polymer membrane. Solubility coefficients as well as diffusion coefficients were satisfactorily correlated with diffusant sizes. Owing to the steric hindrance, branched alcohols have lower solubility coefficient values. The diffusivity exhibited concentration dependent behaviour.

Sefton and Mann\textsuperscript{39} have studied the rate of absorption of benzene by open cell polyurethane foam of varying sizes. The rate of absorption was found to depend on the size of the foam. In order to estimate matrix diffusivities and pore mass transfer coefficients, a dual resistance model was used. There was a good agreement between pore mass transfer coefficients with the order of magnitudes of the steady state resistance for pore diffusion. Therefore, bulk flow is found to be important in the absorption process. Experimental results suggest that the bulk flow was more rapid than pore diffusion. On the basis of experimental results, it was concluded that pore diffusion is more important than bulk flow in foams, giving resistant absorption behaviour which is characteristic of closed cell foams.

Schneider et al.\textsuperscript{40} have investigated the sorption and diffusion of a series of liquids through polyurethane membrane and studied how this behaviour is affected by the choice of solvent and the heterophase nature of the polymer. Sorption experiments in \textit{n}-heptane liquid and incremental sorption experiments in \textit{n}-heptane vapour showed normal Fickian behaviour. With increasing polarity of liquids, the swelling increases to a maximum level. Molar mass between crosslinks computed from the Flory-Rehner equation assuming complete phase segregation varied with different liquids. Oberth\textsuperscript{41} developed a new swelling model for determining crosslink density of polyurethane elastomers. The model is based on the
assumption that every element in the polymer will solvate to the same extent, regardless of whether it belongs to a short or long chain.

Aithal and Aminabhavi\textsuperscript{42} have extensively studied the interactions of industrially important solvents with commercially available polyurethane. They conducted a study on the interaction of halogen substituted organic penetrants with a polyurethane membrane over the temperature interval of 25-60\textdegree{}C. Sorption data have been interpreted in terms of the percentage weight gain of the polymer with respect to time. Except trichloroethylene, sorption was found to increase with increase of temperature. This might be due to the specific interactions of trichloroethylene with the hard segment part of the polyurethane. The diffusivity and permeability values were found to be higher for trichloroethylene and 1,2-dichloroethylene compared to other penetrants, but the solubility of these two penetrants were comparable.

Lawandy and Helaly\textsuperscript{43} investigated the penetration rate of chloroform in chloroprene rubber vulcanisate with different carbon black type and loading. They observed an increase in the penetration rate with the increase in loading percentage. An inverse relationship was noticed between particle size of carbon black and penetration rate, at higher degree of equilibrium. This was attributed to the wrinkles formed at the surface of the rubber at high equilibrium swelling. Chiang and Sefton\textsuperscript{44} used the diffusion analysis to investigate the morphology of styrene-butadiene-styrene (SBS) triblock copolymer. Unlike the diffusion process in conventional rubber, they found that the diffusion of cyclohexane vapour in SBS thermoplastic elastomer exhibits non Fickian time-dependent characteristics. The time-dependent diffusion was attributed to the inability of the polymer molecules to respond instantaneously to the change in concentration. This slow response was due to sorption by the interfacial region at a temperature below its glass transition. The equilibrium diffusion coefficient was estimated to be $3.2 \times 10^{-7}$ cm$^2$/s regardless of the casting surface. According to the sorption measurements, the casting surface did have an effect on the approach to equilibrium. The results
indicated a close packing of the molecules and hence a decreased diffusion coefficient for teflon and glass cast films, because of internal stresses left within the films during casting.

Later Harogoppad and Aminabhavi investigated the interaction of higher alkanes with structurally different elastomer membranes. They looked into the dependence of polymer structure on variations in length of the penetrant molecules. They also found that sorption, diffusion and permeation in these membrane systems were influenced by the nature of the penetrant molecule and the polymer. Penetrant mobility in the polymer and sorption magnitude can be influenced by chain segmental mobility and interactions. For an increase of molecular size from C₆-C₁₆, the sorption rate and sorption magnitude decrease. In all solvents, at higher temperature EPDM showed a less uptake and this has been attributed to the induced crystallinity at higher temperature in the presence of penetrants. The induced crystallinity reduces the free energy of mixing and hence the solvent uptake. Natural rubber also exhibited similar behaviour with 2,2,4-trimethyl pentane. The mechanism of sorption slightly deviates from Fickian to anomalous and this could be supported by slight sigmoidal nature of the sorption curve. The concentration dependency of diffusion coefficient was evident from the significant swelling as shown in Figure 1.2.

The integral absorption and desorption of n-hexane vapour by styrene-butadiene block copolymers were studied as a function of film thickness and vapour pressure at 25°C by Odani et al. These studies indicated that S-B block copolymer films having two different types of morphologies exhibited two non-Fickian features: the thickness anomaly in the reduced absorption and desorption curves and the two-stage absorption curve at a certain concentration. The segmental motions in the PB phase of the copolymers are more restricted than in PB homopolymer, even at a temperature well above the glass transition of the PB blocks. The chain immobilisation effect and the geometric impedance effect due to
the presence of impermeable PS domains interfere with the transport of penetrant molecule in the copolymer solid.

Figure 1.2. Dependent of diffusion coefficient on concentration of solvents for EPDM membranes. [S. B. Harogoppad and T. M. Aminabhavi, Macromolecules, 24, 2598 (1991)].

Iwar and co-workers measured the mutual diffusion coefficients for styrene butadiene rubber (SBR)-n-nonane system by sorption method. The mutual diffusion coefficients were correlated with the free volume theory. Guo et al. designed an experimental method based on a gravimetric permeation cell and successfully used for measuring the diffusivities and permeabilities of several rubber-solvent systems. For the four solvents diffusing in the same rubber, the diffusion coefficients followed the order chloroform > benzene > ethyl benzene > o-xylene. This is consistent with the effect of molecular geometry. The molecule with a greater effective diameter shows a slower diffusion rate in a given polymer. The diffusion in different rubbers follow the trend: silicone > natural > bromobutyl.
This may be related to the difference in fractional free volumes and polymer chain flexibilities in these rubbers.

Malone et al.\textsuperscript{49} have studied the validity of the swelling method for the determination of the interaction parameter by selecting solvents with poly(dimethyl siloxane) (PDMS) using the Flory-Rehner theory and the phantom network assumption. Experiment was carried out on the assumption of the additivity of the free energy of mixing and the elastic free energy of the Flory-Rehner model and the suggestion that the interaction parameter may have dependence on crosslink density in addition to polymer concentration.

Schneider and co-workers\textsuperscript{50} have investigated toluene diffusion in butyl rubber. They have measured sorption isotherm and the polymer mass-fixed diffusion coefficient, $D_1$, for toluene in butyl rubber by the incremental sorption method. The increase in $D_1$ with concentration is strongly exponential to a concentration of 30\% and then begins to level out.

Neuburger and Eichinger\textsuperscript{51} have investigated the applicability of Flory-Rehner theory of swelling by differential swelling measurements on two poly(dimethyl siloxane)(PDMS) networks. The two elastomers are more or less similar in their structure except for the chemical structures of the crosslinks. The samples were swollen in benzene and cyclohexane at 20 and 30°C. The reduced dilation moduli of the two samples parallel to one another in a given solvent at a fixed temperature reveal that solvent and temperature dependence are not encompassed by any known theory.

1.3.2 Diffusion in glassy polymers

Glassy polymers are characterised by hard and brittle moiety with restricted chain mobility. Rotation about the chain axis is limited and motion within the structure is largely vibratory within a frozen quasi-lattice. These dense structures
have very little void space (0.2 to 10%). Therefore diffusion in glassy polymers is more complex compared to that in rubbery polymers.

Choy et al.\textsuperscript{52} investigated the toluene diffusion in highly oriented polypropylene with draw ratios from 1 to 18. Drawing converted the initially spherulitic materials into a fibrous structure with many taut tie molecules lying mainly on the outer boundary of the microfibrils. Thereby the free volume and sorption sites were reduced and the microfibrils become less and less permeable as the draw ratio increases. The diffusivity shows an exponential increase with toluene concentration but the concentration dependence becomes weaker with increasing draw ratio indicating that the severely constrained chain segments in the drawn samples have much less freedom to mix with penetrant molecules. Annealing releases the toluene molecules and thus restores the sorption and diffusion properties to values corresponding to completely relaxed amorphous component, i.e., to values even higher than those of the undrawn but quenched material.

Orchard and Ward\textsuperscript{53} have reported that when the polyethylene tubes were immersed in toluene (liquid) a change in weight was obtained. They have estimated the diffusion rates from these values. They also compared the drawn and undrawn tubes of isotopic homopolymer and copolymer feed stocks. The equilibrium uptake values of the drawn tubes were at least three times lower than those of the feed stock with diffusion coefficient reduced by a factor of twelve or more. New and efficient techniques for estimation of diffusion parameter have been proposed by Ravetkar and co-workers.\textsuperscript{54} They used the moments technique for estimating absorption parameters. This method enjoys advantages such as using the full concentration, time profile and time saving. The validity of these techniques has been demonstrated by the analysis of the data on adsorption of polyacrylamide.

Zielinski and Duda\textsuperscript{55} conducted a study on the self-diffusion of benzene, toluene and ethyl benzene in polystyrene using the Vrentas/Duda free volume diffusion model.\textsuperscript{56,57} Zielinski and Duda\textsuperscript{58} found that predictions of solvent
self-diffusion over ranges of temperature and concentration are in much better agreement with experimental observation than mutual-diffusion coefficients. Diffusion coefficient predictions suggest an exponential concentration dependence of the activation energy required to overcome attractive forces, \( E \). Without the use of any diffusion data, approximating \( E \) as zero over the entire concentration range yields self-diffusion coefficient predictions which are in good agreement with experimental data.

Kim et al.\(^5^9\) measured the self-diffusion coefficient of dodecane in crosslinked polystyrene by means of pulsed gradient spin echo nuclear magnetic resonance (PGSE-NMR) spectroscopy. By using the free volume model of Fujita and Vrentas-Duda, the concentration and temperature dependence of the diffusivity was analysed. Parameters describing the Fujita model were determined from fitting diffusion data to the PVT behaviour of the system. From the analysis of the viscosity of dodecane, the viscoelastic relaxation properties and the glass transition temperature of polystyrene were determined. The parameters describing the Vrentas-Duda model were determined from the diffusion coefficient of the system. Both the Fujita and Vrentas-Duda models described the concentration and temperature dependence of the diffusion coefficient. Diffusion behaviour of two polyimides (PIS) synthesised from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA) and 4,4'-diamino diphenyl sulfone (DDS) were investigated by Moon and Lee.\(^6^0\) The weight uptake of penetrants \( n \)-methyl-2-pyrolidone (NMP) and DMSO showed a linear relationship with time. The mechanism of this phenomenon was considered as the case-II diffusion (Non-Fickian). The polyimine films of the BTDA system had a better affinity to NMP than DMSO since the solubility parameter difference between BTDA-based PIS and NMP is less than five.

Vrentas and Vrentas\(^6^1\) proposed an equation describing sorption behaviour in polymer-penetrant systems. This equation is based on a model that has been formulated for describing the volumetric and sorption behaviour of a system.
composed of a glassy polymer and a penetrant. Later Vrentas and Vrentas evaluated the predictive capabilities of a sorption equation for describing the sorption behaviour of three glassy polymer penetrant systems. They also examined the factors determining the shapes of isotherms for glassy-penetrant systems. Recently, Dragan et al. reported the sorption of phenol, p-toluene sulfonic acid (P-TSA), Na-P-toluene sulfonate (Na-P-TS), 1,2-dihydroxy-3,5-benzene disulfonic and disodium salt (Tiron), and 3-hydroxy-4(sulfonaphthylazo)-5,7-naphthalene-disulfonic acid trisodium salt through the macroporous anion exchangers with acrylamide structural units. The maximum specific sorption of P-TSA was almost identical with the total exchange capacity for both the weak and strong basic anion exchangers. The sorption of Na-P-TS is strongly related to the functional group structure of the anion exchangers.

Brown and co-workers calculated diffusion coefficients of methylene chloride, chloroform, benzene and 2,2,4-trimethyl pentane in 1,4-polybutadiene having trans contents between 2 and 100%. They observed that for amorphous polymers (trans contents less than 70-80%) the diffusion at zero penetrant concentration decreases with increasing trans content and with increasing size of the diffusant.

Spirakis and Rogers have studied the factors contributing to the solubility and diffusivity of penetrants through amorphous polymers. They found that the sorption kinetics change progressively from Fickian to non-Fickian to Case II or Super Case II transport as a function of polymer composition.

1.3.3 Diffusion in polymer blends

The diffusion and transport through polymer blends depend upon its composition. The blends may be heterogeneous or homogeneous. In homogeneous blends, the diffusion process is influenced by the interaction between the component polymers while for heterogeneous blends, interfacial
phenomena and the rubbery or glassy nature of the phases are important. Most polymer blends, however, are heterogeneous and consist of a polymeric matrix in which the second polymer is embedded. Consequently, the effects on permeability are very dependent on the degree of heterogeneity of the system and therefore on the method of formation. The nature and type of polymers used are very important.

The most extensive study of the permeability of rubber blends was perhaps the early work of Barbier. Mesrobian and Ammondson reported the permeability of $n$-heptane and methylsalicylate through polyethylene-nylon blends. Cates and White were among the first to report the sorption behaviour of water in blends of polyacrylonitrile and cellulose, silk and cellulose acetate, respectively. The sorption of water in PAN-cellulose acetate and PAN-cellulose varied linearly with blend composition. However in the case of PAN-silk blend, a complicated sorption behaviour was obtained. Saltonstall and co-workers have reported the desalination of sea water through membrane from blends of cellulose triacetate and cellulose diacetate. Cabasso et al. have investigated the sorption of benzene-cyclohexane mixtures in polymer blend membranes composed of poly(phosphonates) and acetyl cellulose. The authors state that this blend represents a miscible pair. The blend selectively absorbs benzene from benzene-cyclohexane mixtures. They indicated that there was a dramatic concentration dependence of the diffusion coefficient with the increasing concentration of benzene in the blend membrane. Figure 1.3 represents the fractional sorption of benzene from benzene-cyclohexane mixture into poly(phosphonate)-acetyl cellulose blends.
Figure 1.3. Fractional sorption vs. $\sqrt{t}$ for various poly(phosphonate)/cellulose acetate (P/A) blends determined at 30°C from 1/1 (w/w) benzene/cyclohexane mixture: (●) P/A 50, (□) P/A 40, (▲) P/A 30, (○) P/A 20, (■) A (the numbers indicate wt % of P). [I. Cabasso, J. Jagur-Grodzinski and D. Vofsi, J. Appl. Polym. Sci., 18, 2117 (1974).

Hopfenberg and co-workers$^{78-81}$ extensively studied the sorption kinetics and equilibrium of normal alkanes in solution cast blend films of atactic polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The authors systematically examined the effects of temperature, penetrant activity, blend composition and thermal history on the sorption kinetics and equilibria of $n$-hexane in the PS-PPO blends. This blend system has been reported to be compatible over the entire range of blend composition.
Aminabhavi and Phayde have investigated the molecular transport of alkanes through thermoplastic blends of ethylene-propylene random copolymer and isotactic polypropylene. For all liquids, equilibrium penetrant uptake and degree of penetrant overshoot have been influenced by factors such as penetrant size and shape, polymer morphology and temperature. The diffusivity values of 2,2,4-trimethyl pentane at all temperatures were considerably lower than the corresponding values for a linear molecule of similar size, namely, n-octane. This is attributed to the rigidity of 2,2,4-trimethyl pentane. The observed overshoot effect is attributed to the complicated two phase polymer morphology. Also sorption (S)-desorption (D)-resorption (RS)-redesorption (RD) experiments have been performed to determine the sorption equilibrium and transport parameters.

1.4. Membrane based transport process

The feasibility and success of several transport processes depend upon the nature of the membranes used. The development of membranes and its utilisation for the separation of liquid and gas mixtures is an important emerging techniques in membrane science and technology. The membrane morphology dictates the mode of permeation and separation, as shown in Figure 1. The basic morphologies are isotropic (dense or porous) and anisotropic with a tight surface extending from a highly porous wall structure. The tight surface can be dense selective skin, permitting only diffusive transport or a porous skin, allowing viscous flow of the permeates. The membrane separation is achieved by manipulation of these basic morphologies.
1.4.1 **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 process is an emerging membrane separation technique widely used for the separation of organic liquid mixtures. This technique attracted the attention of specialists in chemical, biochemical and petrochemical industries as an energy saving and environment friendly technology.

In pervaporation process, a thin polymer film is brought into contact with the liquid mixture (feed) and the permeant 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 (Figure 1.5). 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. Vacuum pervaporation is the most widely utilised mode of operation, while several other processes such as inert purge pervaporation, thermal pervaporation, perstraction or osmotic distillation, saturated pressure driven pervaporation and electrically induced pervaporation are also available.

![Diagram](image)

**Figure 1.5.** The principle involved in pervaporation process. [M. O. David, R. Gref, T. Q. Nguyen and J. Neel, *Trans. Ichem E.*, 69, 335 (1991)].

Though pervaporation is one of the most popular areas of current membrane research, the concept of pervaporation separation is not new. The phenomenon of pervaporation was first observed by Kober who originated the term in a publication reporting selective permeation of water from aqueous solutions of albumin and toluene through cellulose nitrate films. The usefulness of
pervaporation for separation and concentration was recognised by Farber.\textsuperscript{90} However, the first known quantitative work on pervaporation was published by Heisler \textit{et al.}\textsuperscript{91} for the separation of water/ethanol mixtures using a cellulose membrane. It was the work of Binning and co-workers\textsuperscript{92-94} that established the principles and highlighted the potential of pervaporation technology. In the following years, substantial work was done that widened the research scope to many liquid mixtures and a variety of membranes.

Membranes made of both synthetic polymers and derivatives of natural polymers have been tested for the separation of various liquid mixtures. The applications of pervaporation can be classified into three categories (1) dehydration of organic solvents and their mixtures\textsuperscript{95,96} (2) removal of organic compounds from aqueous solutions\textsuperscript{97,98} and (3) separation of organic liquid mixtures.\textsuperscript{8}

Lee \textit{et al.}\textsuperscript{99} developed various polymer membranes for selective removal of ethanol and chloroform from aqueous binary solution. Flat sheet membranes were cast from polymer solutions and evaluated for their sorption, diffusion and pervaporation of organics from dilute aqueous solutions. Selective sorption of organics dominate pervaporation selectivity of different polymers. Dutta and Sikdar\textsuperscript{100} have shown that ionomeric membranes of perflurosulfonic acid polymer allow selective pervaporation of polar organic compounds from their azeotropic mixtures with less polar compounds. They have also found that fluxes increased with increasing alcohol content of the feed and with temperature. But the selectivity of more permeating component remained reasonably constant around azeotropic point.

Nijhuis\textsuperscript{101} evaluated the pervaporation process, both technically and economically, as a tool for the treatment of effluents. Brun \textit{et al.}\textsuperscript{102} sorbed dilute aqueous solutions of benzene and chloroform on styrene butadiene rubber and nitrile rubber. Several researchers reported on the performance of pervaporation as a tool for the treatment of effluents\textsuperscript{103-105}
Uragami et al.\textsuperscript{106} studied the permeation and separation of benzene-cyclohexane mixtures through liquid-crystalline polymer membrane. The side-chain liquid crystalline polymer (LCP) was synthesised by the addition of the mesogenic monomer to poly(methyl siloxane) using platinum catalyst. They found that permeation rate increased with increasing benzene concentration in the feed solution and permeation temperature. Smolders\textsuperscript{107} reported on the effect of membrane thickness on the removal of trace organics from aqueous solutions. They have used a resistance-in-series model for describing the pervaporation performance of elastomeric membranes. The water fluxes are inversely proportional to the thickness of the actual separating layer and they depend strongly on the type of elastomer used.

The pervaporation performance of poly(alkyl methacrylate)\textsuperscript{108} cross linked with ethylene glycol dimethacrylate (EGDM) membranes was investigated for the separation of benzene-cyclohexane mixtures by Uragami and co-workers. The crosslinked poly(alkyl methacrylate) membranes exhibited benzene permeability for the benzene-cyclohexane mixtures and the permeation rate increased with increasing benzene in the feed solution.

Luo et al.\textsuperscript{109} prepared a membrane by blending cellulose acetate butyrate with cellulose acetate propionate. The properties of these membranes were evaluated by the pervaporation separation of ethyl tert-butyl ether and ethanol mixtures. The experimental results showed that the selectivity and the fluxes of this membrane depend on the blend ratio and on that of the processed feed mixtures.

Neel et al.\textsuperscript{110} have described the high performance exhibited by crosslinked poly(vinyl alcohol)-poly(acrylic acid) blends in the pervaporation and differential permeation of water-alcohol mixtures. Instead of a decrease of permeation flux, an increase in the permeability was observed with PAA crosslinked membranes at low PAA contents. Oliveria et al.\textsuperscript{111} developed membranes from polyacrylonitrile and
polyacrylonitrile-graft-poly(ethylene oxide) blend for separation of water/ethanol mixtures by pervaporation.

A proper understanding of the membrane separation mechanism may provide direct information on the research and development of an appropriate membrane. 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.\textsuperscript{112-114} 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 1.6).\textsuperscript{114}

![Solution-diffusion transport model](image)

\textbf{Figure 1.6.} Solution-diffusion transport model. [J. G. Wijmans and R. W. Baker, \textit{J. Membr. Sci.}, 107, 1 (1995)].

In general, the solubility and diffusivity are concentration dependent. Recently, Matsuura and co-workers\textsuperscript{115-117} 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 1.7).117


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 recognised that the two models represent two different approaches to the description of pervaporation transport.

1.4.2 Vapour permeation

Vapour permeation has emerged as a new industrial membrane technology. In vapour permeation, transport of a condensable vapour through a dense membrane consecutive to an activity gradient takes place. This process offers the unique feature of studying the transport process of a single permeant through a
dense membrane under various upstream activities\(^{118}\). Such characteristics by no means be obtained by liquid permeation, where the modification of the upstream activity of a component can only be achieved by adding another compound to the mixture. The activity of both components is modified in this case in compliance with the Gibbs-Duhem relation, which complicates transport analysis. On the contrary, coupling phenomena are not to be considered with pure vapour permeation results. Furthermore, the calculation of upstream solvent activity demands the use of somewhat complicated vapour liquid equilibria methods. In the case of pure solvent vapour permeation, upstream activity can be easily calculated, provided upstream pressure is precisely monitored\(^ {119}\). This process offers direct practical conclusions for the understanding and rational design of volatile organic components (VOC) vapour recovery from contaminated air streams\(^ {120,121}\). This technique also offers significant opportunities for energy saving and solvent release, compared to classical VOC control processes such as incineration, oxidation or active carbon absorption.

For VOC vapours recovery, as well as organic extraction from aqueous streams by pervaporation, a membrane material showing high organic vapour permeabilities, but low air and water permeabilities is required in order to set up a competitive process: while several elastomeric materials, well known for their high permeabilities as well as organophilic behaviour, have been already proposed for this purpose\(^ {122}\), dense poly(dimethylsiloxane) (PDMS) membranes, commonly named silicone rubber, offer a good compromise in most cases and are widely used\(^ {123}\). Castro et al.\(^ {124}\) analysed the sorption data of hydrocarbon vapours in polyethylene and polypropylene films using, Flory-Huggins, UNIFAC, Michael-Hausslein and Flory-Rehner theories (UNIFAC-FR). Predictions of penetrant activity values through these theories fit quite well the experimental results, with errors ranging between 4.7 and 10.8\%. A typical adsorption isotherm for \(n\)-hexane-polypropylene is shown in Figure 1.8\(^ {124}\).
As can be seen, the solubility depends on temperature and almost linearly on pressure. Duncan and Koros\textsuperscript{125} have measured the permeabilities and diffusivities of methyl chloride and benzene vapours at low activities in 2 mil thick FEP teflon membrane in a continuous flow permeation cell. The permeability and diffusivity were independent of penetrant partial pressures and the permeation process was described by Henry’s law and the sorption by Fickian diffusion model. The diffusion and permeation coefficients of \textit{n}-alkanes (from carbon atom numbers 12 to 32) have been measured by the pouch method for LDPE, HDPE, polypropylene copolymer and polypropylene homopolymer.\textsuperscript{3,126,127}

Salwinski \textit{et al.}\textsuperscript{128} developed a method for simultaneous determination of \textit{D}, \textit{P} and \textit{S} of organic vapour through polymers from the mass transport. A kinetic equation was developed to estimate the loss of vapour under constant pressure in relation to mass transfer near zero pressure. Sorption of methanol vapours in Estrofol and polythermopolyester films was investigated.\textsuperscript{129} The sorption capacities
of degassed and non-degassed films were similar. The permeation of propane, propene, ethane and ethylene through 0.0051 cm thick polyethylene films was determined from 25 to 30°C.\textsuperscript{130} The S and D of acetylene, ethylene, ethane, propane, butane, pentane and xenon in poly(trimethyl vinylsilane) were determined by the sorption-desorption method in the pressure range of 0-700 torr.\textsuperscript{131}

The permeability coefficients of benzene vapours in air from the measured values of solubility and diffusivity for natural rubber, neoprene, a blend of natural rubber and neoprene, butyl rubber, poly(vinyl chloride) and polyethylene membranes were calculated.\textsuperscript{132} The permeability for natural rubber at room temperature was $4.2 \times 10^1$ cm$^2$/s for 10 ppm concentration of benzene vapour in air.

Vapour sorption technique is also a good tool for the thermodynamic characterisation of polymer blends. Analysis of equilibrium sorption of a vapour by the blend can provide information regarding polymer-polymer interactions.\textsuperscript{133-135} The amount of vapour sorbed is related to its interaction with the blend. By comparing this interaction with the interaction between the vapour and each of the pure polymers it is possible to obtain information about the interaction between the polymer components of the blend.

Recently, Geuskens\textsuperscript{136} has investigated the morphology of polyethylene-silicone blends by combining scanning electron microscopy with measurements of permeability to methanol vapour and selective extraction of the silicone phase by diethylether. He found that in polyethylene-silicone blends, SEM and permeability measurements are complementary sources of information regarding the morphology of the blends. SEM is useful to characterise the microstructure of the blends at low silicone content. He also found that the permeability measurements are useful to determine how phase inversion proceeds and what composition of the blend corresponds to the maximum level of co-continuity of the two phases.
1.4.3 Gas permeation

Gas transport through polymers is an area of growing interest as materials with unique transport properties continue to find use in new, specialised applications ranging from extended life tennis balls\textsuperscript{137} to natural gas separation systems. The ability to relate polymer molecular structure to gas transport properties is crucial in any attempt to rationally design materials for specific permeability applications such as gas barriers. Historically, the availability of experimental permeability data has been limited mostly to common/commercial polymers\textsuperscript{138} and the information demonstrated that gas transport rates of polymers may vary by many orders of magnitude. A variety of techniques has been used to measure gas permeation through polymer membranes. The most common method utilises a Dow permeation cell wherein the film is sealed in the cell. The downstream side of the chamber is evacuated and the test gas is passed upstream at a given pressure to reach equilibrium with the film while maintaining vacuum on the downstream side. The film must be dry since the method does not differentiate between the test gas permeating the polymer sample and water vapour.

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.\textsuperscript{139-143} The permeating species interacts with the polymer matrix and selectively dissolve 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 1.9 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.\textsuperscript{144} In viscous flow, flow is inversely proportioned 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.\textsuperscript{145} Ultra micro porous molecular sieving membrane has higher productivities and selectivities than solution diffusion mechanics.\textsuperscript{146,147}

![Diagram of gas molecules](image)

**Figure 1.9.** Mechanism of flow of gas molecules: (a) viscous flow, (b) Knudson flow, (c) molecular sieving and (d) solution-diffusion. [J. R. Fried, *Polymer Science and Technology*, Prentice Hall, Englewood, Cliffs, New Jersey, 1995, Ch. 12, p. 427].

The gas sorption to 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. Recently, a more complex BET-type sorption isotherm which describes multilayer sorption has also been discussed. 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\textsuperscript{148-152} (Figure 1.10).\textsuperscript{153} The gas transport behaviour for glassy polymer is then described by a so-called dual mobility model,\textsuperscript{154,155} 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\textsuperscript{156-158} 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.$^{159,160}$ 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.

By comparison, 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 homogenise 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. 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. On the other hand, porous membranes usually have very high permeabilities but their selectivity is generally low. Kanitz and Huang investigated the permeation of gases through poly(ethylene styrene) grafted copolymer membranes prepared by γ-ray irradiation. They also studied separation of nitrogen and methane gases in air using vacuum-irradiated polyethylene and teflon FEP films. Rogers studied the permeation and separation of helium and nitrogen gases through a grafted methyl methacrylate and polyisoprene membrane.

Haraya and Hwang have conducted permeation studies in a series of 19 polymers for selecting appropriate polymer for the separation of O$_2$/Ar mixtures. The gas permeabilities and diffusivities in all polymer tested are in the order O$_2$ > Ar > N$_2$. Higher permselectivities are observed in glassy polymers than in rubbery polymers. Permeability ratios for O$_2$/N$_2$ in glassy polymers are strongly affected by the contribution of the diffusivity ratios. Recently, Lai and co-workers studied the transport phenomenon of oxygen and nitrogen across a pure polycarbonate and a cobalt(III) acetylacetonate [Co(acac)$_3$] containing polycarbonate membrane. Co(acac)$_3$ was added into a polycarbonate membrane to enhance its oxygen solubility. It was found that oxygen permeability increased slightly with respect to pressure.

The gas transport in polymer blend is directly affected by the morphology and chemical uniformity of the material. For instance, the enhancement of the permselectivity of a membrane composed of a miscible polymer pair, over that of membrane composed of the parent polymers, was
demonstrated with poly(dimethylphenylene oxide)-polystyrene blend. Using the ratios of the permeabilities of the pure gases, the separation factor for the gas pairs He-CH$_4$ and CO$_2$-CH$_4$ was estimated. For both pairs, the estimated separation factor passes through a prominent maximum, indicating that the blend membrane is significantly more selective than expected from the behaviour of a two-polymer component (Figure 1.11).171

![Figure 1.11](image)

**Figure 1.11.** Separation factor for He-CH$_4$ pair at 1010 kPa (10 atm) 35°C, as computed from the permeability coefficient of the pure gases in PPO-PS blends. [Y. Maeda and D. R. Paul, *Polymer*, 26, 2055 (1985)].

Ranby and co-workers have reported the most extensive experimental study of permeability behaviour in polymer blend systems. Ranby focused his early work on mechanical blends of poly(vinyl chloride) (PVC) with ethylene-vinylacetate copolymers (EVA) and with acrylonitrile-butadiene copolymers (NBR) respectively. The effect of varying vinyl acetate content on the miscibility of the resulting blends and in turn, on the transport behaviour was the primary
focus of the study. Recently, Wang et al.\textsuperscript{175} reported on the gas sorption and transport properties of the membrane from polycarbonate/Co(III) acetyl acetonate blend. Various amounts of cobalt(III) acetyl acetonate (Co(acac)_3) were added to polycarbonate (PC) membrane to enhance its oxygen enrichment ability.

Even though several polymer membranes are available for separation process nowadays, only a few of them exhibit high selectivity and permeability. Hence the pursuit is still going in both laboratory and industry for the development of membranes with high permeability and high selectivity.

1.5. Scope of the work

Styrene-butadiene rubber (SBR) is a general purpose rubber which has many applications. The high filler loading capacity and good flex resistance of SBR make it useful in several engineering and industrial areas. Natural rubber (NR) is a well-known polymer that has been widely used in a variety of industrial and engineering applications. Nylon 6 is an engineering plastic characterised by its high tensile strength and resistance to hydrocarbons. EPR is a speciality rubber characterised by its ageing and weathering properties. A polymer blending concept was used to make new membranes. Thus SBR/NR and nylon/EPR blends were prepared. A detailed investigation on the solvent sorption behaviour of SBR, NR, SBR/NR blends, nylon, EPR and nylon/EPR blends is necessary for the possible use of these membranes as barrier materials.

As a first step in developing membranes based on SBR, it was vulcanised by four different vulcanisation techniques. Thus four different types of crosslinks are introduced between the rubber chains. The nature as well as the distribution of crosslinks controls the overall properties of the end products. Therefore, the influence of nature of crosslinks, degree of crosslinking, penetrant size and temperature on the sorption characteristics of SBR were examined in detail. The mechanical properties of unswollen, swollen and deswollen styrene-butadiene
rubber samples were evaluated. Nature of crosslinks was characterised by both physical and chemical methods.

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 filler. The flexibility and free volume of the network decrease considerably with increase in reinforcement. Transport characteristics depend on the degree of reinforcement. Also, filler reinforced materials exhibit high strength compared to gum vulcanisate, which is essential for the smooth functioning of membranes. Hence it is relevant to look into the effect of particle size, shape and structure of the fillers on the transport process.

Permeation behaviour of immiscible blends is strongly influenced by its morphology. Therefore, the relationship between morphology and transport characteristics of nylon/EPR blends was examined.

The solvent sorption characteristics of styrene-butadiene rubber/natural rubber blends have been studied and explained in terms of the mode of crosslinking, the magnitude and distribution of crosslinks between the rubber chains, morphology, blend ratio, penetrant size, temperature etc. We have also looked into the relationship between dynamic mechanical behaviour and transport characteristics of SBR/NR blends. In addition to this, the mechanical behaviour of unswollen, swollen and deswollen samples was also examined.

The temperature susceptibility of rubber vulcanisates depends on the nature and distribution of crosslinks, the nature of the filler and its reinforcing efficiency. Therefore, much attention has been given to study the influence of temperature on the transport process through SBR, NR, SBR/NR blends, nylon 6, EPR and their blends. The nature of the penetrant is very important in a transport process. Its characteristics such as size, shape, molecular weight and polarity decide the equilibrium sorption values as well as the values of transport coefficients.
The experimental observations have been used to estimate different kinetic parameters such as diffusion coefficient, sorption coefficient permeability coefficient and thermodynamic parameters such as enthalpy, entropy, activation energy and rubber-solvent interaction parameter. These parameters are very important for developing clear theoretical generalisations regarding the interaction of elastomers with different liquids.

The feasibility of utilising SBR, NR and SBR/NR blend membranes for the separation of organic liquid mixtures by pervaporation technique has been examined. The influence of factors such as blend ratio, feed composition, nature of crosslinks and penetrant size on the separation process has been analysed. Sorption, diffusion and permeation of organic vapours through SBR, NR and SBR/NR blends were carried out with respect to blend ratio and nature of crosslinks. The permeation of organic vapours through nylon/EPR blends has also been investigated in detail. Further, the permeation results have been used to compliment the observation from scanning electron microscopy.

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, finally the permeation behaviour of SBR, NR and SBR/NR blends was analysed with oxygen and nitrogen. The motive behind this study is to investigate the possible use of SBR/NR blends as a new membrane system for the oxygen and nitrogen separations.
1.6. References


