INTRODUCTION

I.1. POLYMERIC GEOMEMBRANES vs ENVIRONMENT

I.1.1. Geomembranes as Liners

Polymers have been used as geomembranes in a variety of underground applications. These serve as liners in hazardous waste chemical ponds and other related areas. Before we discuss the various types of polymers used as geomembranes, we will first outline the environmental conditions under which these geomembranes are used. The term “hazardous waste” has crept into our vocabulary during the past decades and it denotes waste that presents risk to human health and hygiene. Both organic and inorganic chemicals are found in waste dumps, but organics are the most feared complex substances that pose threat to human health and environment. According to a recent survey [1], industrial organic wastes are the largest class in hazardous chemicals. Since most of the organic chemicals have been dumped into landfills, incineration, the technology developed to deal with the destruction of organic wastes, is often not practicable.

The term ‘chemical waste’ refers to industrial or laboratory chemicals having corrosive, toxic, flammable or explosive properties. Among all the developments in hazardous waste regulation, the restriction on land disposal exerts
the most profound and widespread impact on waste management practices. Many industrial wastes are currently disposed in unregulated landfills and this will continue to grow despite reduction efforts [2] (see Table I.1). Most landfills have an average useful life of 20 years. During this time and often for many years (up to 200 years or so), chemicals from the wastes may migrate into the fertile soil below the landfill. Once within the landfill, they may react with other materials producing leachates and gases that are highly toxic. If the concentrations of toxic chemicals in water are below their taste-odor threshold, then people are likely to be exposed to chemicals by drinking such water [3, 4]. Safety precautions in the form of protective clothing to the operator on landfills are needed and this hazard can be minimized by a judicious choice of the protective polymeric barrier [5].

Polymers in various forms and shapes to meet the demands required in hazardous waste treatment have been developed. In this respect, geomembranes made from polymers have proven to be resistant to the environmental and chemical degradation reactions while at the same time maintain their physical, mechanical and chemical properties [6]. The last decade has witnessed a tremendous growth in the development of newer polymers that provide the desired functions necessary for the construction of hazardous waste storage facilities at a lower cost when compared to the previously used natural construction materials [7]. In such applications, polymers have been selected based on the laboratory test data and confirmed by testing under simulated conditions of use. Chemical resistance of a polymer is its ability to withstand the chemical attack with a minimum change in appearance, dimensional stability, mechanical properties and mass over an extended period of time.

Geomembranes are impervious thin polymeric sheets used primarily as liners. Their primary function is always as a liquid or vapour barrier. The range of
applications is quite large and at least 30 individual applications in civil engineering have been developed. The geomembrane are prepared from both thermosetting and thermoplastic polymers. Some synthetic rubbers other than natural rubber are also used as geomembranes. However, the original geomembrane used as a pond liner was butyl rubber, a copolymer of isobutylene with approximately 2 % isoprene.

Geomembranes are used in a variety of areas as a liner for: (i) protecting potable water and reserve water, (ii) to avoid transport of waste liquids (acidic and basic), (iii) resisting to low level radioactive wastes, (iv) solar ponds and (v) brine solutions in addition to primary, secondary and/or tertiary hazardous waste landfills. They are also used as floating reservoirs for seepage control and floating reservoir covers to prevent pollution in addition to controlling odours in landfills.

The three tests that are commonly performed on geomembranes used in landfill liner applications are: (i) conformance testing, which demonstrates the applications of the material to be met for a solid waste facility, (ii) chemical compatibility testing, which determines whether the geomembrane is compatible with leachate generated and (iii) quality assurance/quality control testing, which assures that installation of the geomembrane liner meets all the specifications and regulatory requirements. Table I.2 summarizes the major types of polymers used as geomembranes [8].

Potential service life of geomembranes is important when solid hazardous waste landfills are to be lined with these materials. It is therefore, necessary to know the aging characteristics and the potential service life of polymers used as geomembranes. But, it is difficult to compare the published results from different laboratories due to different processing methods employed. Even though many
polymers are used as geomembranes, their choice is narrowed when aggressive liquids are to be contained. Organic solvents, phenols and a host of other chemicals are reactive to most polymers with the possible exception of polyethylene.

Table I.1

Growth in waste volume from 1977 to 1999 despite reduction efforts [2].

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Average annual growth (millions of tons)</th>
<th>% Increase during</th>
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<tbody>
<tr>
<td>Heavy metals</td>
<td>51 114 149 196  7.6 5.5</td>
<td></td>
</tr>
<tr>
<td>Organic chemicals</td>
<td>42 100 132 180  8.2 5.7</td>
<td></td>
</tr>
<tr>
<td>Petroleum products</td>
<td>16 33 44 60  6.8 5.9</td>
<td></td>
</tr>
<tr>
<td>Inorganic chemicals</td>
<td>17 35 43 55  6.8 4.2</td>
<td></td>
</tr>
<tr>
<td>Other hazardous wastes</td>
<td>5 9 13 19  5.5 7.6</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>131 291 380 510  7.5 5.5</td>
<td></td>
</tr>
<tr>
<td>By method of disposal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill/surface impound</td>
<td>12 200 225 165  29.1 2.4</td>
<td></td>
</tr>
<tr>
<td>Treatment/stabilization</td>
<td>2 13 50 150  18.5 30.9</td>
<td></td>
</tr>
<tr>
<td>Incineration</td>
<td>a 15 35 95  - 18.5</td>
<td></td>
</tr>
<tr>
<td>Resource recovery</td>
<td>2 15 30 75  17.7 20.1</td>
<td></td>
</tr>
<tr>
<td>Deep-well injection</td>
<td>5 14 15 10  9.8 1.4</td>
<td></td>
</tr>
<tr>
<td>Illegal disposal</td>
<td>110 35 20 5  -9.9 -10.6</td>
<td></td>
</tr>
<tr>
<td>Other methods</td>
<td>a 2 5 10  - 20.1</td>
<td></td>
</tr>
<tr>
<td>a-negligible</td>
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</table>
Table 1.2

Major types of polymers used as geomembranes [8]

<table>
<thead>
<tr>
<th><strong>Thermoplastic polymers</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl chloride) (PVC), High and low density polyethylenes (PEs), Chlorinated polyethylene (CPE), etc.</td>
</tr>
<tr>
<td>Elasticized polyolefin, Polyamides (nylons)</td>
</tr>
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<table>
<thead>
<tr>
<th><strong>Thermoset polymers</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene-isobutylene (butyl), Epichlorhydrin rubber, Ethylene propylene diene monomer (EPDM), Polychloroprene (neoprene), Ethylene vinyl acetate (EVA)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Combinations</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC-Nitrile rubber, PE-EPDM, PVC-EVA, Crosslinked CPE, Chlorosulfonated polyethylene (CSM), also called “Hypalon”</td>
</tr>
</tbody>
</table>

Research efforts over the past decades have shown that there has been a great swing from rubber to polyethylene for use as a basic raw material for liners used in hazardous waste applications due to its superior chemical resistance, high strength and low cost. These include linear low-density polyethylene (LLDPE), which has good stress resistance, flexibility and resistance to hydrocarbons when compared to high-density polyethylene (HDPE). Ultra linear low-density polyethylene (ULLDPE), an improvement on LLDPE, is almost a rubber-like flexible product. HDPE copolymers or combinations with the above materials or rubber-based materials, which are aimed at maintaining HDPE’s overall chemical resistance, offer the improved stress crack and flexibility. HDPE has been the most resistant geomembrane to a large number of chemicals including most...
inorganic and organic acids as well as salts, but is only mildly attacked by some aggressive organic liquids.

A variety of polymeric geomembranes have been used in different landfill applications. August [9] developed a method to determine the residual permeability of geomembrane liners for landfill applications. This method was based on the permeation cell evaluation with dilute aqueous solutions and landfill leachates. Several materials as landfill sealers involving the addition of bentonite have been developed [10]. Of the synthetic sealers, HDPE is the most suitable for base sealing of landfills. Friescke [11] described specifications for geomembrane landfill liners in relation to their physical and chemical resistance. Schlutter [12] made some useful suggestions about the proper installation of polymeric landfill liners under varied weathering conditions. By using a suitable polymeric liner in landfill applications, it was possible to avoid the leachate migration.

The properties and test methods used for geomembranes and their failure due to oxidative photodegradation, biodegradation, radiation, mechanical or chemical degradations have been discussed earlier [13-22]. Brittle fracture, including various forms of stress cracking, fatigue and slow crack growth in polyethylene (PE) geomembranes have also been studied. To minimize the brittle cracking failures, factors such as thermal contraction stress, residual stresses in seams, mechanical damage to the geomembrane, synergism of chemicals and stresses are to be evaluated. Different test methods to measure liquid permeation through geomembranes in complex mixtures of waste liquids are important.

Harrocks and D’Souza [23] studied different types of degradation processes under different environmental conditions for several geomembranes. Lord and Halse [24] have also studied the factors that cause polymer degradation.
Cadawallader [25] discussed different factors involved in accelerated aging and studied the degradation mechanism of HDPE liners under the influence of heat, UV light, high energy radiation, environmental stress, biological organisms, chemicals and oxygen. In all these cases, degradation occurred mainly due to the rupture of primary and secondary chemical bonds in HDPE chains. Dudzik et al [26] suggested the use of HDPE and PVC geomembranes as landfill liners due to their good chemical compatibility and no material degradation caused by exposure to leachate. In another study by Dudzik and Tisinger [27], the chemical compatibility of HDPE geomembranes exposed to industrial waste leachates for up to one year has been evaluated using the EPA test method 9090. The leachates tested were the dissolved metals and salts. The infrared spectral data indicated that organic constituents of the leachates were not significantly absorbed into geomembrane and no degradation of geomembranes occurred.

Lord and Koemer [28] discussed the fundamental concepts on the chemical degradation of geomembranes as studied by water vapour transmission, radioactive tracer transmission, water and water vapour sorption. Diffusion parameters were evaluated and discussed in terms of the possible degradation reactions. The UV-stabilized polyethylene membranes to be used as liners for landfills were studied by Schmidt et al [29]. The effect of film thickness, UV-light, ambient temperature and microbial attack on PVC geomembranes have been studied [30]. Doyle and Baker [31] conducted the weathering exposure tests on five geomembranes for waste impoundment and secondary containment of storage tanks. The five membranes tested were: HDPE, Du Pont’s Hytrel (a polyester elastomer), a urethane-coated polyester, oil-resistant chlorinated polyethylene and oil-resistant grade PVC. After two years, HDPE and Du Pont Hytrel were unaffected, but a polyurethane-coated polyester showed signs of moderate degradation, while chlorinated HDPE and oil-resistant PVC were severely degraded.
In an attempt to investigate the strength and durability of the presently available seaming systems, 37 combinations of reinforced and nonreinforced polymeric membranes joined by various seaming methods were subjected to organic chemical mixtures, brine and water immersion, freeze/thaw cycling, wet-drying, heat aging and accelerated outdoor aging tests [32]. Polymer membranes used in this study were: HDPE, LLDPE, EPDM, PVC, CPE and Hypalon. The chemicals were chosen to represent a wide range of groups including organic and inorganic acids, bases, halogenated hydrocarbons, ketones and aldehydes. Evaluation was done before and after mechanical testing of the seams (dynamic load in shear and peel, and static dead load) using gas chromatography (GC). These results were useful for field engineers, geomembrane fabricators and other regulatory bodies during the groundwater pollution prevention studies [33]. Polymers used in this study were: LLDPE, HDPE, elastomeric polyolefin blend, PVC and butyl rubber.

There are numerous factors that require consideration in the design and construction of landfill barriers as proposed in several papers and review articles [34-40]. Rowe [41] has recently discussed the effect of: (i) temperature in landfills, (ii) the clogging of filters in leachate collection systems and their service life, (iii) service life issues related to compacted clay liners, geosynthetic clay liners and geomembrane liners, (iv) diffusion and attenuation of contaminants in liner systems, (v) leakage through composite liners and (vii) stability of barrier systems.

The temperature in leachate collection system can have a significant effect on the rate of clogging and service life of any geomembrane liner [42-46]. Other implications are related to the rate of contaminant diffusion through low permeability liners (i.e., geomembrane, compacted clay or geosynthetic clay
liners). Figure 1.1 displays the temperature variation with distance in gas and leachate collection pipe at an operating landfill [46]. The exposure conditions of a geomembrane are dependent upon whether it is part of a composite, primary or secondary liner. As a component of the primary liner, the geomembrane is subject to direct contact with leachate and temperatures higher than normal groundwater temperatures. Thus, the service life of geomembranes varies depending upon the external conditions [47].

It was shown that the temperature at the base of the landfills is particularly sensitive to the type of waste, rate of landfilling and the saturated thickness of waste. In particular, leachate on the base of the landfill (e.g., due to clogging of a leachate collection system or failure to remove leachate from the collection system) may result in a significant increase in temperature at the landfill liner. This will increase the contaminant diffusive transport through the liner system, which can reduce the service life of both the geomembrane as well as the underlying compacted clay liner.

1.1.2. TEST METHODS FOR GEOMEMBRANES

Several test methods have been used for the evaluation of geomembranes, but a unified approach is not available. These methods have been subdivided as: (i) physical, (ii) mechanical, (iii) hydraulic, (iv) endurance, (v) chemical resistance and (vi) environmental. A good coverage on various test methods is given elsewhere [7]. Two important physical property tests involve specific gravity and thickness. Mechanical property test methods determining compressibility, tensile strength, fatigue strength, burst strength, tear tests, impact tests, puncture tests and soil-to-fabric friction are highly relevant. The environmental property test
Fig. I.1. Temperature variation with distance in gas and leachate collection pipe at an operating landfill in Germany [46]
methods are used to recognize the potential problems and limitations of using polymeric fabrics. The ASTM D453 test method, under the title “resistance of plastics to chemical reagents”, includes reporting changes in mass, dimension, appearance and strength. Provisions are also made for various exposure times with different reagents at elevated temperatures.

Parallel to the developmental activities in the experimental methods, theoretical models have also been developed to understand the transport of small molecules through polymer membranes. Existing literature suggests that transport depends on polymer structure, its morphology and nature of the penetrant molecules. Therefore, small molecules have been used as probes to explore the detailed mechanism of transport into dense polymer matrices. One of the main goals to study sorption and transport of liquids into polymer membranes is to evaluate the diffusion and permeation parameters [48, 49]. These parameters are dependent upon solvent concentration and temperature. Several numerical schemes and modeling procedures have been developed to study solvent diffusivity as a function of concentration [50-59]. However, the concentration independent diffusivity can be calculated from the simplified Fick’s equation before the completion of 55 % equilibrium sorption.

Compared to sophisticated experimental techniques including nuclear magnetic resonance imaging, laser interferometry, etc. [60-65], the sorption gravimetric method was also found to be good for studying liquid transport into polymer membranes [66-77]. A gravimetric payne cup method has also been used to measure the permeation rates of liquids [78-82], but these methods require large polymer samples and work well for the aqueous penetrants. Research in the area of molecular transport of liquids into polymeric sheet membranes is still being
actively pursued [83-86]. However, it is beyond the scope of the present thesis to cite all these references and only representative references are discussed.

I.1.3. CHEMISTRY AND TECHNOLOGY OF GEOMEMBRANES

Different polymeric geomembranes have been used by the field engineers depending upon their specific end uses. In the present thesis, we have used four geomembranes: (i) polypropylene, (ii) very low-density polyethylene (DURA SEAL VL), (iii) linear low-density polyethylene (DURA SEAL LL) and (iv) high-density polyethylene (DURA SEAL HD). These membranes were received from National Seal Company (NSC), Galesburg, IL, USA. A brief introduction on the preparation, properties and applications of these geomembranes will be discussed.

I.1.3.1. Polypropylene (PP)

There are two types of polypropylenes (isotactic and syndiotactic). Isotactic PP can be prepared in two different ways. One, by bubbling propylene through a catalyst suspension prepared by treating titanium tetrachloride and tri-isobutylaluminium in decahydronaphthalene or lithium aluminium tetradecyl and titanium tetrachloride in cyclohexane and precipitating the product formed by isopropanol. The other by using a Ziegler and Natta catalyst. Isotactic PP is prepared by bubbling propylene at 40 psi pressure over the catalyst prepared by treating diethylaluminium chloride and titanium trichloride in n-heptane. Isotactic PP stands as an introduction to enormous contributions made by Giulio Natta (stereoregular polymers) who shared the Nobel Prize with Ziegler for this work.
Syndiotactic PP is prepared by passing the high purity propylene over a mixture of anisole, vanadium tetrachloride and iso-dibutylaluminium chloride in toluene at -78 °C, and precipitating the final product in methanol. The melting temperature of isotactic and syndiotactic PP are 166°C and 188-200°C, respectively although it varies with steric purity.

Polypropylene is used in petrochemical, agrochemical, pulp and paper mills, steel and aluminium plants, semiconductor manufacturing and many other industries. Its other uses include: O-rings, valves, mechanical seals and controllers, plate type heat exchanger gaskets, pipes, diaphragms, flexible joints, hose, insulation/jacketing for wire and cable, etc.

I.1.3.2. Polyethylenes (PE)

Ethylene polymerizes to a high molecular mass, branched polyethylene with a melting point ranging between 110 and 135°C, depending upon the extent of branching. Low-density polyethylene was first prepared in 1933 by a free radical polymerization at high pressures and temperatures. High-density polyethylene is prepared by using a titanium-based catalyst at an atmospheric pressure. The PE prepared by using titanium catalysts has a high density with low degree of branching. Polyethylene prepared at high pressure using free radicals will vary in properties from a nearly linear, high-density product to highly branched, low-density material, depending upon the polymerization conditions.

Polyethylenes provide several benefits such as resistance to a wide variety of chemicals, service in high temperature environments and excellent electrical resistance properties. These polymers offer good resistance to acids, bases, steam/hot water, hydraulic fluids of all types, brake fluids, oils and lubricants.
amine corrosion inhibitors, oxidizing agents, bleaches, alcohols and various industrial solvents. They also provide good resistance to radiation, weathering and ozone.

1.2. MEMBRANES IN PERVAPORATION SEPARATION

The separation of azeotropic organic mixtures, stereoisomers, industrially important solvents like dimethylsulfoxide, dimethyl formamide, iso-propanol, tetrahydrofuran, etc., from their aqueous or organic mixtures is a tedious task due to their closely boiling points or their identical chemical structures/natures. The separation of such liquids from their mixtures using the conventional distillation and extraction processes are expensive. On the other hand, the membrane-based separation processes (MBSPs) are environmentally clean, efficient and less expensive when compared to the conventional methods of separation. The MBSPs have been used to produce potable water from saltish sea water [87, 88], to treat industrial effluents [89], to fractionate, concentrate and purify solutions in chemical and pharmaceutical industries in addition to separation of stereoisomers. In all these applications, membranes are the key elements. Practical MBSPs include reverse osmosis, electrodialysis, micro-, ultra- and nano-filtrations in addition to gas separations [90]. However, pervaporation (PV) separation has been rated as an efficient, energy saving and environmentally clean technique used to separate of organic-organic and aqueous-organic mixtures. A multitude of different types of membranes have been used in PV.

Membrane morphology is also important in controlling the mode of permeation and separation. The basic morphologies are isotropic (dense and porous) and anisotropic with a tight surface extending from a highly porous wall.
structure. The tight surface can be a dense selective skin permitting only the
diffusive transport or a porous skin, allowing the viscous flow of the permeants.
Membrane separation is therefore achieved by manipulating the basic
morphologies in polymers.

In PV separation, membrane acts as a barrier, which selectively permeates
one component of the mixture, while the other component is retained. Thus, for a
PV process to be successful economically, two key parameters are important: (i)
selectivity of the membrane i.e., its ability to differentiate between the components
of a mixture such as between water and alcohol or between ions and water and (ii)
efficiency of the membrane i.e., the flux achieved under a given set of
experimental conditions. The pre-requisite for flux i.e., for material transport
through membrane, is the driving force. Also, the membrane structure is very
important. An efficient membrane should be highly resistant to heat, pH, solvent
and mechanical degradation.

Contrary to other membrane processes such as nano-filtration and ultra-
filtration, a phase transition occurs during PV. Consequently, the energy input of
the process is at least equal to the heat of vapourization of the permeating liquids.
The PV technique was first developed in the Research Center of the American Oil
Company in Texas in the late fifties and early sixties [91-93], even though Kober
[94] was responsible for coining the word "pervaporation". Unlike other
membrane processes such as reverse osmosis, ultra-filtration and micro-filtration,
no large-scale industrial PV units existed until recently. The main reasons for this
are: (i) the need for energy-intensive vapourization of the mixtures and (ii) the bad
performance obtained with the commercial membranes. Thus, research efforts to
prepare efficient membranes began in seventies and eighties for the development
of PV process on a large-scale.

Chapter I
There are two main approaches to describe mass transport in PV experiments: (i) solution-diffusion model and (ii) pore flow model. According to solution-diffusion model, liquid components are sorbed into the membrane, diffuse through it and desorb or evaporate as vapours on the downstream side of the membrane. Okada et al [95-97] proposed a transport model to analyze PV data on the basis of pore flow mechanism based on: (i) liquid transport from the pore inlet to a liquid-vapor phase boundary, (ii) evaporation at the phase boundary and (iii) vapor transport from the boundary to the pore outlet. An interesting feature of this model is that it assumes a liquid vapor phase boundary inside the membrane and PV was considered to be a combination of both liquid transport and vapor transport in series.

In PV experiments, flux is usually a permeation flux, $J$ (expressed as kg/m$^2$.s or kg/m$^2$.h) which is a measure of selectivity and is usually calculated by knowing the mass fractions of components in the feed mixture as well as in the permeate. The flux and selectivity are governed by mass transport through membrane. These parameters are very sensitive to changes in feed composition. With liquids, separation is achieved because membranes have the ability to transport one component more readily than the other, even if the driving forces are equal. Hence, prediction of selectivity is often difficult due to the coupling of fluxes, i.e., the permeation rate of one component can be changed due to the movement of other component. Thus, in a PV experiment, separation is achieved when the permeation flux is created by maintaining the downstream pressure lower than the atmospheric pressure. This is achieved by creating vacuum on the downstream side or by employing a carrier gas as shown schematically in Fig. 1.2.
Fig I.2. Schematic representation of the PV separation.
Formation of ethanol by fermentation of biomasses that are rich in sugar and starch are the most important industrial PV processes. The liquid product is an aqueous solution, which contains 5 % ethanol that is separated by distillation to give 95 % ethanol. This is an energy intensive step, which accounts for a large portion of the cost of ethanol production from biomass. The PV technique is an economical and energy-saving alternative process for water-ethanol separation. Most publications on membrane separation of aqueous ethanol mixture by PV deal with the separation by a selective permeation of water [98-104]. Some reports are also available on the separation by selective permeation of ethanol [105-109], but the separation factors in these studies were less than 20. Research efforts on PV dehydration of organic solvents have promoted further research [110-119]. For ethanol extraction, the selectivity obtained by PV hardly exceeds that obtained by a simple vapourization; i.e., selectivity is nearly 12 for a feed containing 5 % ethanol.

An exceptionally higher selectivity than vapourization has been obtained with silicone-grafted polymers [120], styrene-fluoroacrylate copolymers and silicalite filled silicone films [121]. Removal of low molecular mass organics from dilute aqueous mixtures is usually based on volatility or sorption between these compounds and water. Although air stripping and carbon adsorption are commonly used, these processes exhibit low selectivity and often transfer organics to the vapor phase. PV is used for such difficult separations. In an assessment of potential energy savings by fluid separation techniques, PV was ranked the third highest among the 31 other techniques employed [122].

Pervaporation has been studied theoretically by several researchers. Earlier, Long [123] described the steady-state permeation process by Fick's law with a concentration-dependent diffusivity. Later, Fels and Huang [124-126] developed a
model to predict separation factors and permeabilities based on the free volume theory of Fujita [127]. However, the agreement between theory and agreement is inadequate, particularly for the case assuming independent permeation. Lee [128] used the solution-diffusion model with concentration-independent diffusion coefficients and without considering any mutual interaction of the mixture components and interaction with the membrane. Greenlaw et al [129] studied the effect of linear relationship between the concentration of permeants and their diffusion coefficients for ideal liquid mixtures.

Brun et al [130, 131] developed a "six coefficient exponential model" which is an extension of the Long model [123]. However, by this model it was difficult to predict selectivity and permeability for any mixture. Rautenbach and Albrecht [132], in their model, used diffusion coefficients that have linear relationships with concentration of both components of the mixture diffusing within the membrane. In this model, like that Brun et al [130, 131], prediction of selectivity was not possible. Recent models, which take into account the interactions between liquid components and the membrane material by following Flory's theory appear to be more realistic to narrow down the difference between the predicted and the measured properties [133, 134]. This type of research is still under active progress in many laboratories.

On the experimental side, a variety of membranes have been developed and these are classified as microporous, dense, and composite. The latter is a combination of the former two. Charbit et al [135] focused their attention on the first two kinds of membranes. Microporous membranes exhibit a high permeability, but their selectivity is poor. However, the opposite situation characterizes the dense (or homogeneous) membranes. In general, experimental and theoretical work on PV has been divided into three main groups. The first and
the most important one deals with the relation between chemical composition of the membrane and its selectivity or permeability to separate a given mixture [136-143]. The second category deals with the measurements of diffusivity and solubility of liquids inside the membranes [144-153]. In the third category, studies are related to the development of new apparatus and process design [136, 147, 154-157]. These can be considered as macroscopic approaches of the phenomenon involved in the transfer of solute from liquid phase to gas phase. This way of considering the transfer leads to an evaluation of permeability, breakthrough time or the overall mass transfer coefficient, which are a global representation of several phenomena involved in the mass transfer processes [158-161].

I.2.1. PERVAPORATION MEMBRANES IN DEHYDRATION

Major application of PV separation is in the dehydration of organic liquid mixtures and separation of azeotropic mixtures such as water/ethanol, water/acetic acid, etc. Several PV dehydration membranes have been prepared in the literature [162-170]. Many hydrophilic membranes like poly(vinyl alcohol) [171], cellulose, polysaccharides [172], polyion complex consisting of poly(acrylic acid) and polycation, sulfonated polyethylene, poly(hydoxymethylene), poly(maleimide-co-acrylonitrile) and poly(sulfone-amide) [173], etc. have been used in the dehydration studies of organics from their aqueous mixtures.

The objective of this thesis is to develop water permselective membrane with high selectivity and good permeation flux. As the hydrophilicity of the membrane increases due to higher interactions between the membrane and the mixture rich in water, the membrane swells so that selectivity is reduced. In order to maintain an appropriate balance between selectivity and permeation flux, many
methods have been devised to prepare polymers by crosslinking the active polymer, polymerizing active monomer onto an inert polymer, grafting an active/inert polymer onto inert/active polymer, etc. The research in this direction is still actively going on.

I.2.2. PERVAPORATION MEMBRANES IN ORGANIC-ORGANIC MIXTURE SEPARATION

Several polymer membranes have been prepared and used in the separation of organic liquids from their mixtures. For example Kusakabe et al [174] have prepared a polyurethane-silica hybrid membranes for the selective separation of benzene from its mixture with cyclohexane. For the selective separation of methanol from its mixture with methyl tert-butyl ether, Ray et al [175] have used the copolymer membranes of hydroxyethyl methacrylate, methacrylic acid and vinyl pyrrolidone with acrylonitrile backbone. Kottayam research group [176, 177] has also studied the PV separation of organic-organic mixtures. In addition, there are many other studies related to organic-organic separation and these can be found in the literature [88].

I.3. STUDY ON POLYMER-SOLVENT INTERACTIONS BY INVERSE GAS CHROMATOGRAPHY

Transport of low molecular mass liquids within polymers is an important area of research which exerts a tremendous influence on such technologies as processing of additives in polymers, membrane preparations, transport of
biologically active molecules through polymer membranes/matrices in controlled release (CR) areas and many others [178-184]. In all these studies, solubility and diffusivity are the key parameters that are frequently required to design newer methods for polymer synthesis and fabrication operations.

In polymer manufacturing processes, sorption and diffusion of volatile components from concentrated polymer solutions or polymer melt are critical because these limit the efficiency and hence, the economics of the process. Typical examples include solvent devolatilization, residual monomer stripping, packaging, drying of paints and coatings. However, the conventional methods of measuring these properties rely heavily on the bulk equilibrium measurements and gravimetric sorption/desorption experiments, but these methods pose limitations to polymer-solvent systems when the solvent is present in vanishingly small amounts or at temperatures in the vicinity of or below the glass transition temperature ($T_g$) of the polymer. The longer sorption time and lower diffusivity values, characteristic of the polymer-solvent systems at these conditions, are the causes of experimental difficulties encountered in the classical methods. Accuracy suffers because even a small amount of solute cannot be detectable quantitatively.

As a consequence, there is a need for accurate data on solubility and diffusivity of common solvents in commercially important polymers. Such information has been routinely obtained in the literature using the gravimetric method [185-193]. However, in recent years, due to the pioneering research of Munk and coworkers [194-203] as well as Guillet et al [204-206], intensive research efforts have been focused on the use of inverse gas chromatography (IGC) as an alternative method to study the interaction of polymers with the volatile liquids.
In IGC, the polymer is used as a stationary phase in the chromatographic column and the probe liquid is vapourized and injected into a carrier gas flowing through the column. As the probe transports through column, it interacts with the polymer by the process of adsorption or absorption. From a measurement of retention time of the probe and the shape of the elution profile (i.e., chromatographic peak), the strength and nature of interactions between polymer and probe molecule can be assessed. This experiment is called IGC to differentiate it from the more common analytical gas chromatography (GC).

Due to advances made in IGC method, it is now possible to measure solvent diffusion coefficients as low as $10^{-13}$ cm$^2$/s on polymer (or polymer blend) systems of interest in a relatively short time. IGC is not only useful to test the diffusion theories, but also to study the effects of temperature, solvent size, molecular structure and $T_g$ on the diffusion process. Such data can be compared with those obtained from the conventional techniques. The IGC method has an additional advantage of estimating activity coefficients at infinite dilution, Henry's law constants of volatile organics as well as many thermodynamic parameters of interest. Investigations in this area have been actively pursued by a number of researchers [207-209]. Recently, several reports have appeared on the study of polymer-solvent interactions using IGC [210-214].

1.4. RESEARCH PROBLEM OF THE THESIS

The present thesis is concerned about the experimental and theoretical studies on molecular transport of liquids through polymer membranes and to understand the polymer-solvent interactions. Our investigations fall into three categories. In the first phase, structurally different geomembranes have been used
to study their interactions with a variety of organic liquids that are generally found as waste chemicals in hazardous sites. The geomembranes used are: (i) polyethylenes (PE) of different densities viz., high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE) and (ii) polypropylene (PP). The interactions have been studied by a measurement of sorption/desorption, diffusion and permeation of liquids into these membranes. An effort was made to correlate these properties with the structural variations of the membranes and the liquid penetrants. Realizing the temperature dependence of transport properties, Arrhenius activation parameters were calculated for different transport processes. Furthermore, Fick's equation was employed to compute the concentration profiles of liquids into the sheet membranes.

In the second phase of this research, new acrylamide grafted poly(vinyl alcohol) i.e., both hydrophilic/water selective membranes have been developed and used for the effective separation of water/dimethyl formamide mixture. Effect of membrane morphology (in terms of percentage of grafting) and thickness was investigated for water permselectivity from its mixture with DMF. Effect of diffusion, temperature and permeation flux on pervaporation separation was investigated. Similar PV separation results are presented for acetic acid/water system using PVA-g-PAAm membranes.

The third phase of our research activity is centered around the development of IGC method to study the polymer-penetrant interactions. Attempts have been made to estimate the diffusion coefficients as well as other thermodynamic parameters of interest. Here, experiments were performed on polystyrene in which polystyrene was used as a stationary phase to study the interactions of the alkanes acting as mobile phase.

Chapter I
The present thesis thus aims at a comprehensive understanding of the overall molecular transport phenomenon at a fundamental level and then use this information in technological areas such as in hazardous waste treatment, pervaporation separation as well as in accurately predicting the polymer-penetrant interactions. The systems selected in this research are new and the thesis is advancement toward understanding the molecular transport phenomena.
1.5. REFERENCES


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