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PREPARATION AND CHARACTERIZATION OF POLYMER-ZEOLITE COMPOSITE MEMBRANES

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ABSTRACT

This thesis is on the investigation of polymer-zeolite composite membranes for gas separation and the effects of a number of parameters such as solvent and zeolite type, zeolite content, polymer/solvent ratio and preparation temperature on the microstructure of the final membrane. Although there is an increasing interest in polymeric composite membranes, most of the previous work concentrated on the synthesis and performance measurements of new membrane materials rather than the effects of different methods and parameters on processing.

In this study polymer-zeolite composite membranes were prepared by a phase inversion technique. Polysulfone, natural zeolite and synthetic zeolite 13X were used as polymer and second phases respectively. Dichloromethane and dimethylformamide were used as solvents. Four experimental sets of membranes containing the same polymer but different solvents and zeolites with increasing zeolite loadings were prepared and characterized by thermogravimetric analysis, infrared spectroscopy, optical microscopy and scanning electron microscopy.

It has been found that the types of the solvent and zeolite directly affect the final microstructure of the membranes. Solvent removal rate and distribution of zeolite particles are important and have strong effects on the mechanical performance of the membranes. Membranes prepared by using synthetic zeolite 13X and dichloromethane were determined to be the best zeolite distributions in the microstructure by optical microscopy and thermogravimetric analysis. Uniform and mechanically strong membranes with 20-60 % synthetic zeolite contents were prepared. Mechanically weak and relatively nonuniform membranes were prepared by using natural zeolite clinoptilolite. The incorporation of an ultrasonic treatment of the zeolite dispersion most likely contributed in the successful deagglomeration of the second phase in the polymer matrix.

ÖZ

Bu çalışma gaz ayırma işlemleri için polimer zeolit kompozit membranların hazırlanması ile çözücü ve zeolit cinsi, zeolit miktarı, polimer/çözücü oranı, ve hazırlama sıcaklığı gibi parametrelerin membranın mikroyapısı ve performansı üzerindeki etkisinin incelenmesini içerir. Polimer ve polimer komposit membran teknolojisi üzerine giderek artan bir ilgi olmasına rağmen bu alanda daha önce yapılan çalışmalar membran hazırlama teknikleri ve hazırlama parametrelerinin etkisinden daha çok yeni membran malzemelerinin üretimi ve bu membranların performanslarının ölçümleri üzerinde yoğunlaşmıştır.

Polimer-zeolit kompozit membranların hazırlanmasında faz dönüşümü tekniği kullanılmıştır. Polimer olarak polisülfon, çözücü olarak dimetilformamid ve diklorometan, zeolit olarak hem doğal hem de sentetik zeolit kullanılmıştır. Hazırlanmalarında farklı çözücüler kullanılan, aynı polimeri ancak farklı zeolit cinslerini değişen oranlarda içeren membranlardan oluşan dört ayrı deney seti hazırlanmış, bu membranların karakterizasyonu ısısal analiz sistemi, IR spektroskopisi, optik mikroskop ve taramalı elektron mikroskopu kullanılarak yapılmıştır

Sonuç olarak sentetik zeolit 13X ve diklorometan kullanılarak hazırlanan membranların, en iyi zeolit dağılımına sahip oldukları optik mikroskop ve ısısal analiz çalışmalarıyle tespit edildi. %20-60 sentetik zeolite içeren, homojen ve mekanik olarak sağlam membranlar hazırlandı. Mekanik olarak zayıf ve göreceli olarak homojen olmayan membranlar doğal zeolit kullanılarak hazırlanan membranlardı. Zeolit süspansiyonu hazırlanması sırasında ultrasonik banyo kullanımının, polymer matriks içinde zeolitlerin homojen dağılımına yardımcı olduğu saptandı.

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Chapter I

INTRODUCTION

Membrane is a permselective interphase between two bulk phases. These bulk phases may be homogeneous or heterogeneous; nonporous, microporous or macroporous solid, a liquid phase or a gel. The membrane phase is always thin with respect to the two bulk phases.

In a membrane separation process, the membrane phase controls the exchange of mass between the two bulk phases which are mixtures. One of the species in the mixture is allowed to be exchanged in preference to others. The membrane is selective to one of the species. One of the bulk phases is enriched in the species which is preferentially transported. Selective and controlled transfer of one species from one bulk phase to another bulk phase separated by the membrane is accomplished during the process.

The transport of species across the membrane is due to one or more driving forces. These driving forces are generated by a chemical potential gradient or electrical potential gradient. A gradient in chemical potential may be due to a concentration gradient or pressure gradient or both. The flux of any species through the membrane per unit driving force is proportional to the permeability of the species. The driving force can be expressed as the partial pressure difference Δp_i or the concentration difference Δc_i across the membrane, for species i,

flux of species i =[(permeability of species i)/membrane thickness)] (Δp_i or Δc_i).

The ratio, [(permeability of species *i* / effective membrane thickness)], is called the normalized permeability of species *i* in membrane separations. There are a couple of ways to define the selectivity of the membrane between two species. A common definition for the separation factor α_{ij} (sometimes called as the selectivity) for species i and j is;

$$\alpha_{ij} = (c_i''/c_j'')/(c_i'/c_j')$$

where the prime and double prime superscripts refer to the upstream bulk phase (feed) and the downstream bulk phase (permeate) respectively. If downstream pressure or concentration is negligible in comparison to the upstream pressure or concentration, the separation factor will be equal to the ratio of permeabilities of the two species.

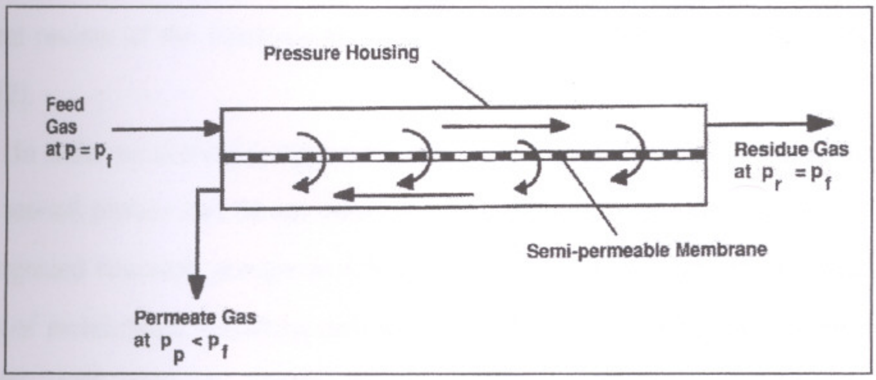

Figure 1. A typical membrane based separation application [1].

Although commercial membrane applications became available in the late 1970's, the membrane concept in separation was known by scientists in 1800s. Since all the necessary separations and mass transport processes in living organisms are based on membranes, they attracted significant interest especially from biologists and physiologist. The scientific descriptions of osmosis and dialysis were given by Dutrochet in 1823. Traube and Pfeffer made quantitative studies on osmosis in 1867 and 1877. Graham produced oxygen enriched air by using membranes by the end of the 19th century.

The first well-known membrane based separation process was their use for the separation of uranium isotopes and UF_6 utilizing inorganic porous membranes. This was part of the Manhattan Project which led to the development of the first nuclear weapons during World War II. Research and development on membranes continued on laboratory scale without a significant industrial application until 1970s.

Development of polymer science and polymer engineering enabled scientists and engineers to prepare new membranes by using polymers such as polysulfones, polyacetates etc. In mid 1970s, Monsanto announced their first commercial polymeric membrane (Prism™) for gas separation and other commercial membranes became available especially for water desalination by reverse osmosis. Successful transfer of the experience gained to other large-scale separation processes made membrane separation processes become a promising alternative to conventional separation techniques. Gas separation membranes became commercially available for O_2, N_2, CO_2, CO, H_2, and CH_4 separation by 1980s. Since the dominant part of any membrane process is the membrane itself, academic and industrial interest have been focused on the new membrane materials that exhibit high permeability and high selectivity to the components of interest. An excellent review of the fundamentals of membrane science is given in a review paper by Stern [2].

In order to achieve a high permeability without decreasing the selectivity or vice versa, second phases can be introduced into polymeric membranes. There are a number of recognized research groups in USA and Europe. Koros et al. [3] examined a large variety of membranes including polyamides, polysulfone, cellulose acetate, other glassy polymers, and polymer blends in separation processes such as gas separation, desalination, and reverse osmosis. They also examined the effects of aromatic and functional groups on the performance of the membranes. They found that different functional groups may have a direct effect on the membrane performance. Duval [4] examined the performance of different polymeric matrix membranes with zeolites, silicalite and carbon fillers. EPDM and PDMS filled membranes were prepared and the effect of adsorbent type and loading on the membrane performance for gas separation and pervaporation were evaluated. It was also found that permeabilities of specific gases and liquids first decrease with the adsorbent loading then increase above a certain loadings. An increase in the performance was observed generally in all filled membranes depending on the filler type and loading. He concluded that separation performances of rubbery polymers were significantly enhanced when zeolites were incorporated provided that the gas molecules could diffuse through the zeolite particles. This effect was polymer independent and was even observed when non-selective or poorly permeable polymers were considered. Hennepe [5] reported improved selectivities for the separation of various alcohols from water by pervaporation using silicalite filled silicone rubber membranes. Yilmaz [6] and Okumus [7] studied the effect of feed composition on the performance of membranes and the separation of water-alcohol mixtures by pervaporation in polymer-zeolite mixed-matrix membranes respectively. Their results showed that selectivity was independent of feed composition indicating that ternary interactions did not effect the gas permeation mechanism. Zeolite additions may increase permeability but may also cause a small decrease in selectivity. The preparation procedure and the zeolite type significantly affected the transport properties of membranes in this work. Almost all of these studies used phase inversion technique to produce polymer or polymeric mixed-matrix membranes. Gur [8] used extrusion techniques to prepare zeolite filled polysulfone membranes for gas separation. He found that addition of zeolite did not increase membrane performance significantly. In Li's [9] study, a new approach was applied to produce very thin polymeric membranes. In this technique polymer is dissolved in a solvent with a suitable surface tension and a density lower than that of water. Then the solution is fed on water. As the solvent evaporates very thin, 1 to 10 nm, polymeric film is formed on the surface of water. The membrane produced by this technique has very good gas separation performance and can be produced continuously.

In this study the preparation of polymer-zeolite composite membranes for gas separation and the effects of a number of parameters such as solvent and zeolite type, zeolite content, polymer/solvent ratio and preparation temperature on the microstructure of the final membrane have been investigated.

Chapter II

MEMBRANE TYPES AND THEIR CLASSIFICATION

Since synthetic membranes have significant differences in their physical and chemical structures, it is a difficult task to classify membranes. Classifications mostly take into account one property of membranes. Membranes can be divided into three groups with respect to structure, material and application. A classification in line with the above fact was prepared by the author of this thesis and is schematically given in Figure 2. An alternative classification based on the structure, production method, function and application showing the basic relation between different combinations is given in Figure 3.

2.1 Structure Based Classification

2.1.1 Asymmetric Membranes

The most widely used membranes used nowadays in separation processes have asymmetric structures. A membrane basically is required to have high mass transport rates for desired components and good mechanical strength. An asymmetric membrane consists of a very thin (0.1 to 1 μm) layer on a highly porous 100- to 200-μm-thick sublayer. The very thin skin is the actual membrane. This is schematically shown in Figure 5. The separation characteristics and performances are determined by the nature of this skin layer or the pore size. The mass transport rate mainly is determined by the thickness, since it is inversely proportional to the thickness of the actual barrier layer. The highly porous sublayer serves as a support for the very thin and fragile skin and has very little effect on the separation characteristics and the mass transport rates of the membrane.

Asymmetric membranes are used primarily in pressure-driven membrane processes like reverse osmosis, ultrafiltration, or gas separation where high mass transfer rates and good mechanical properties are required.

In addition to high filtration rates, asymmetric membranes have another significant advantage. Conventional symmetric structures act as asymmetric depth filters and retain most particles within their internal structure. These trapped particles plug the membrane and the flux decreases during operation. Asymmetric membranes are surface filters retaining all rejected materials at the surface where they can be removed by shear forces applied by the feed solution moving parallel to the membrane surface. The difference in the filtration behaviours of symmetric and asymmetric membrane are shown schematically in Figure 5.

Composite membrane may also have an asymmetric structure. The actual selective membrane layer is deposited on the surface of a porous substrate. The performance of a composite membrane is not determined only by the selective surface layer but also the microporous support structure, pore size, pore distribution and overall porosity.

The porosity of the microporous substructure should be as high as possible to minimize the proportion of the surface film that is in contact with the support in order to maximize mass transport area. The pore diameter should be as small as possible to minimize the distance between unsupported points of the polymer layer for better mechanical strength of the top layer.

2.1.2 Symmetric Membranes

A homogeneous membrane consists of a uniform dense film or porous layer through which a mixture of species is transported under pressure, concentration, or electrical potential gradients. The transport rates of various species through the membrane depend on their diffusivities and concentrations in the membrane. Separation is accomplished through the differences in these transport rates. Since the transport of species occurs by diffusion and the permeabilities are relatively low, homogeneous membranes should be as thin as possible. These membranes may also separate species similar in size and diffusivities with different solubilities or concentrations in the membrane.

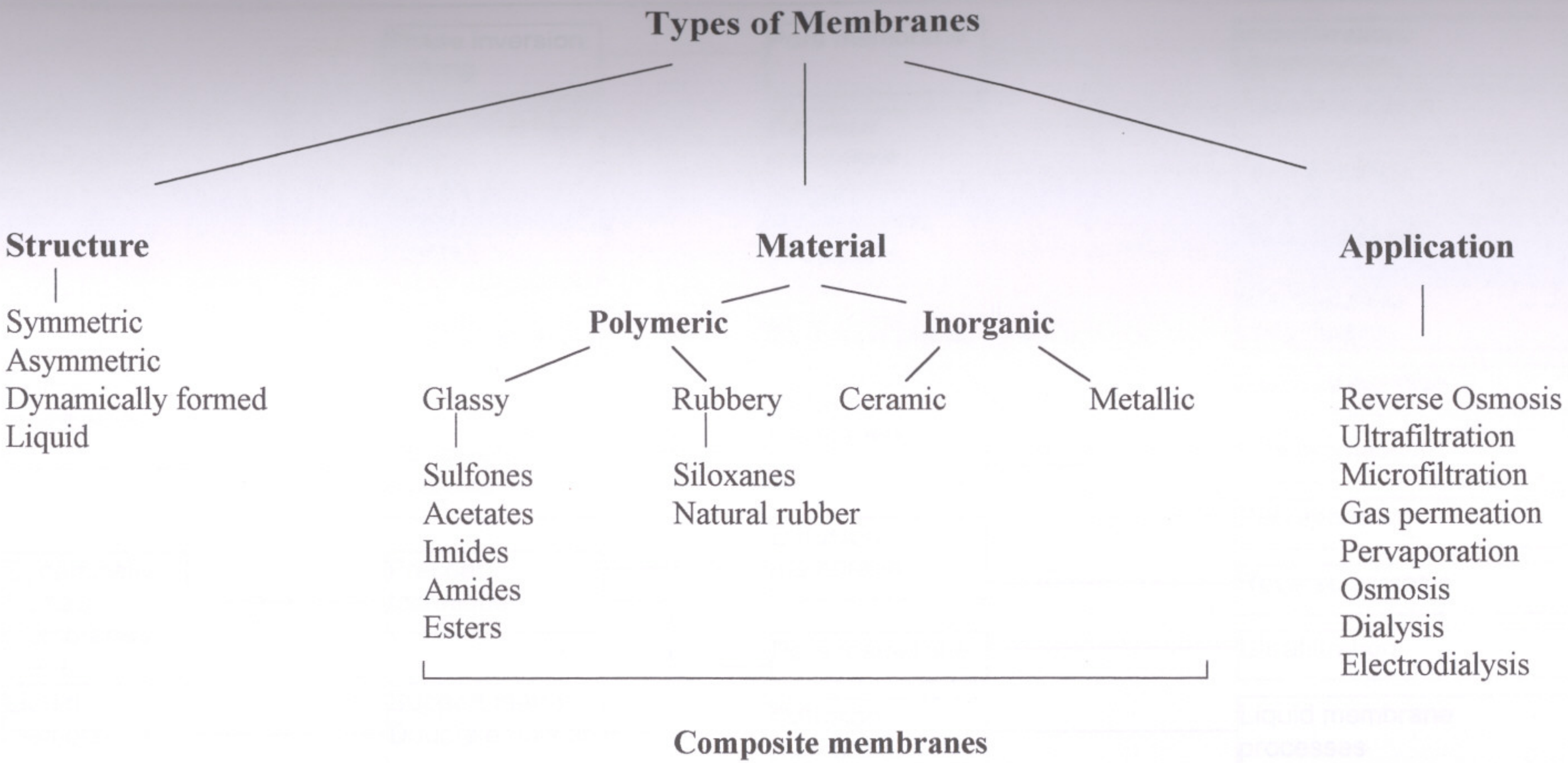

Figure 2. Classification of membranes based on their structure, material, and application.

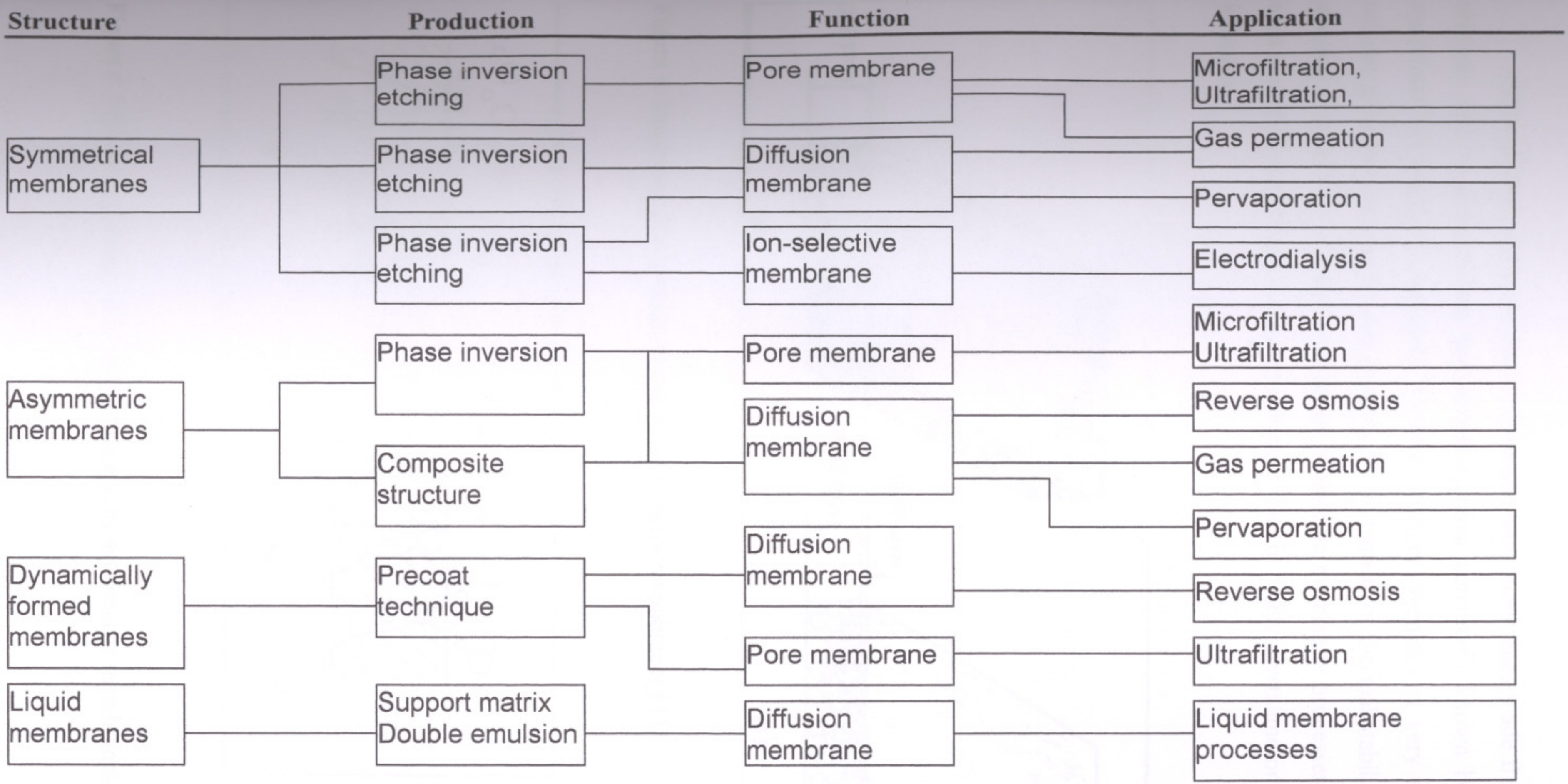

Figure 3. Classification of membranes according to structure, function and production method [10].

Although there are a number of homogeneous membranes made from inorganic materials such as glass, metals and ceramics, most commonly known homogeneous membranes are polymeric materials. Modern polymer chemistry is very successful in tailoring polymers for specific uses in terms of mechanical or thermal stability as well as chemical compatibility to satisfy the needs of specific membrane processes. In general, mass transfer is greater in amorphous polymers than in highly crystalline or cross-linked polymers.

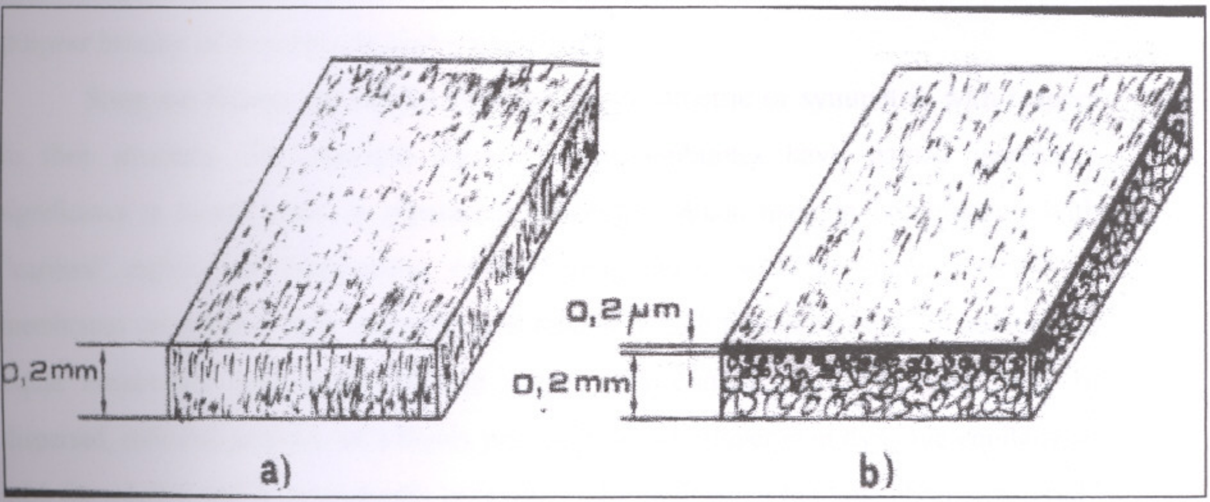

Figure 4. Structures of a) symmetric and b) asymmetric membranes [11].

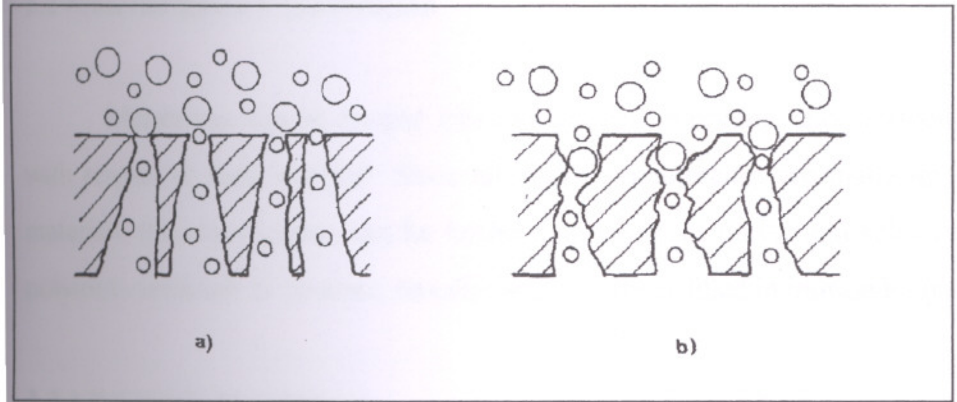

Figure 5. Filtration behaviour of a) symmetric and b) asymmetric membranes

Thus crystallisation and orientation are undesired properties for polymeric membranes. A highly crystallized and oriented structure is not desired in polymeric membranes. On the other hand crystallinity, cross-linking and the degree of orientation enhance the mechanical properties of polymeric materials. The membrane will represent a compromise between necessary strength properties and desired mass-flux. The principal aim is to create a barrier which has the necessary mechanical properties without pinholes or defects and as thin as possible

Homogeneous membranes are used in various applications. The most important ones are gas separation and pervaporation. Silicon rubber is the most widely used polymer because of its relatively high permeability.

Some membranes can not be classified as asymmetric or symmetric with respect to their structure. For example liquid phase membranes have gained increasing significance in recent years in separation processes. When used in combination with "carriers" capable of transporting certain components, such as metal ions, these membranes can achieve high selectivity and relatively high transport rates. In addition to liquid membranes dynamically formed membranes consist of a selective layer of dispersed, colloidal particles on a highly porous base. This layer is in dynamic equilibrium with the solution and is permanently removed and rebuilt since the "membrane material" is suspended in the feed solution to be separated.

2.2 Material Based Classification

Membranes can be divided into two groups as organic and inorganic membranes with respect to their material. Since all organic membranes are made up of polymeric materials, this classification can be further improved as glassy and rubbery polymers in polymeric materials or ceramic, metallic and adsorbent filled in inorganic materials.

2.2.1 Polymeric Membranes

Polymers are large molecules built up by the repetition of small, simple chemical units. This repetition may be linear or branched to form the three-dimensional networks.

Glassy polymers such as polysulfones, polyamides, polyacetates are in glassy state at room temperature so the membranes made up of these materials have glass like properties and have high selectivities and low permeabilities. Rubbery polymers such as natural rubber, silicon rubber and siloxanes are in rubbery state at room temperature. They show rubber like properties and membranes made up of rubbery polymers show high permeabilities but low selectivities

2.2.2 Inorganic Membranes

Ceramic, metallic and adsorbent filled composite membranes may be grouped under this heading. The application of ceramic membranes in separation processes has received considerable attention in the past few years because of their high chemical, mechanical, and biological stabilities in comparison with polymeric membranes. Ultrafiltration alumina, titania and zirconia membranes are commercially available porous ceramic membranes. The high-temperature properties of these membranes are currently attracting considerable interest for their potential high-temperature applications. Like ceramic membranes, metallic membranes are preferred for their high-temperature and high-pressure mechanical and chemical stabilities.

In order to prepare membranes with high permeability and high selectivity inorganic materials such as zeolites, active carbon, or other molecular sieves can be introduced in to a polymeric matrix. These membranes may also be called composite membranes too. Although composite membranes usually have a layered structure, adsorbent filled composite membranes consist of a polymer matrix and a second phase distributed in the matrix.

2.3 Application Based Classification

Membranes with different physical properties and structures may be used for the same separation processes. Most important membrane separation processes are listed in the Tables 1 and 2. Some of these membrane based separation processes are briefly discussed below.

Osmosis is a separation process in which the solvent is transported through the membrane as a result of a difference in trans-membrane concentration [10]. The separation is based on osmotic equilibrium which is a hydrodynamic equilibrium: solvent still passes through the membrane but fluxes are statistically the same in both directions. Although application of osmosis are limited some aqueous solutions can be separated into their components by osmosis.

In reverse osmosis an external force which is greater than corresponding osmotic equilibrium is applied and the solvent flux is reversed so that the solution with greater concentration is further concentrated [10]. If the membrane retains only macromolecules or particles with an insignificant osmotic pressure the process is termed as ultrafiltration. Some applications of reverse osmosis and ultrafiltration are: separation of proteins, treatment of special process effluents in the chemical, food, textile and paper industries, sea and brackish water desalination and concentration of emulsions and enzyme solutions.

Microfiltration is a separation process in which very fine colloidal particles in the micrometer and submicrometer range can be removed from liquids and gases but hydrodynamics of the feed flow is very different from “dead-end filtration” and “cross-flow filtration”. Separation of emulsions, pre-treatment for reverse-osmosis, and concentrating and/or washing of various colloidal suspensions are the main application areas of microfiltration.

In dialysis the flux of dissolved lower molecular mass components through the membrane as a result of a difference in trans-membrane concentration occurs [10]. Dialysis is generally applied with osmosis in normal operation, thus reduces the concentration of the initial solution. Usually, NaOH recovery, removal of alcohol from beer and especially the treatment of patients with chronic kidney disease are the main application areas of dialysis.

Electrodialysis utilize ion-selective membranes and an electric field orthogonal to the membranes. The anions in the solution in the inter-membrane compartments pass through the anion-exchange membrane under the influence of the electric field and the cations through the cation-exchange membrane. Electrodialysis is particularly economical for desalination of brackish water, preliminary concentration of sea water for salt recovery, and demineralisation of whey.

Pervaporation is a membrane process in which a phase change occurs during material transport. The driving force is the reduction in activity on the permeate side. This is in general realized by applying a vacuum at the permeate side. Pervaporation is more expensive with respect to other processes. Consequently, pervaporation is limited to cases where traditional methods are very costly, e.g. separation of isomers or mixtures with an azeotropic point.

Gas mixtures can be separated with porous and with 'dense' membranes. Material transport through the membrane is realised in gas permeation by a trans-membrane pressure difference of up to 70 bar. Gas separation membranes and polymeric materials for gas separation will be described in detail in the next two chapters.

Table 1. The most important membrane separation processes [10].

Membrane Process	Separation Potential for	Driving force realised by	Preferably permeating component
Reverse Osmosis	Aqueous low molecular mass solutions Aqueous organic solutions	Pressure difference (< 100 bar)	Solvent
Ultrafiltration	Macromolecular solutions, emulsions	Pressure difference (< 10 bar)	Solvent
Microfiltration	Suspension, emulsions	Pressure difference (< 5 bar)	Continuous phase
Gas permeation	Gas mixtures, water vapour-gas mixtures	Pressure difference (< 80 bar)	Preferably permeating component
Pervaporation	Organic mixtures, aqueous-organic mixtures	Permeate side: ratio of partial pressure to saturation pressure	Preferably permeating component
Liquid membrane	Aqueous low molecular mass solutions, aqueous-organic solutions	Concentration difference	Solute (ions)
Osmosis	Aqueous solutions	Concentration difference	Solvent
Dialysis	Aqueous solutions	Concentration difference	Solute (ions)
Electrodialysis	Aqueous solutions	Electric field	Solute (ions)

Table 2. Membrane separation processes [11].

Separation process	**Membrane type**	**Driving force**	**Method of separation**	**Range of application**
Microfiltration	Symmetric microporous membrane 0.1 to 10 µm pore radius	Hydrostatic pressure difference 0.1 to 1 bar	Sieving mechanism due to pore radius and absorption	Sterile filtration clarification
Ultrafiltration	Asymmetric microporous membrane 1 to 10 nm pore radius	Hydrostatic pressure difference 0.5 to 5 bar	Sieving mechanism	Separation of macromolecular solutions
Reverse osmosis	Hydrostatic pressure 20 to 100 bar	Hydrostatic pressure difference 20 to 100 bar	Solution-diffusion mechanism	Separation of salt and microsolutes from solutions
Dialysis	Symmetric microporous membrane 0.1 to 10 nm pore radius	Concentration gradient	Diffusion in convection free layer	Separation of salt and microsolutes from macromolecular solutions
Electrodialysis	Cation- and anion-exchange membranes	Electrical potential gradient	Electrical charge of particle and size	Desalting of ionic solutions
Gas separation	Homogeneous or porous polymer	Hydrostatic pressure concentration gradient	Solubility, diffusion	Separation of gas mixtures

Chapter III

GAS SEPARATION MEMBRANES

One of the most exciting and significant unit operations applied in recent years is the membrane based separation of gaseous mixtures. Although it is a new technology, it has found acceptance in a range of industrial, medical, and laboratory applications. A gas separation membrane separates gaseous species and is very different from filtration of gaseous mixtures. In a gas separation process the components to be separated are gas molecules whereas in gaseous filtration they are gas molecules and solid particles. Typical gas separation applications include air separation (O_2 and N_2 enrichment), recovery of helium, dehumidification, removal of impurities from natural gas, hydrogen recovery from refinery and petrochemical streams, and recovery of carbon dioxide.

Gas membranes function in environments quite unlike those of other applications, such as pressures of up to 2000 psi and temperatures of up to 200 ^{0}C may be needed. These harsh conditions delayed the commercial development of gas separation membranes. The nature of gas separation also demands that membranes be as defect free as possible because small pinholes affect the separation far more than they do in other membrane processes. The earlier systems offered by some companies were not widely accepted but when Monsanto introduced its Prism system in 1979, gas separation membranes really became commercially attractive.

Membrane technology was used in industry for many years. Developments in this area led to emerge membranes suitable for industrial gas separations. Membrane gas separation can compete with cryogenic distillation, adsorption and absorption processes such as pressure swing adsorption. Membranes can also compete with the on-site production of gases such as oxygen and nitrogen.

The most important advantage of gas membranes is the simplicity of their installation and operation. Rotating parts or circulating liquids are not involved, so supervision and maintenance costs are at a minimum. In many applications, membranes have lower capital costs. They are generally compact which is important in transportation. Membrane processes are flexible and additional capacity is easily added to an existing plant. They are environmental friendly because they contain no toxic liquids.

The yield of a membrane separation system is proportional to the pressure difference and the surface area but inversely proportional to the thickness. The separation of a gas mixture that can be achieved is a function of the selectivity coefficient and the pressure ratio through the membrane. Up to 1980's, all membranes for gas separations were polymeric and the thinnest practical membranes were in 50-100 μm thick. Membrane packages consisted of a stack of flat sheets. The investment for a separation process based on this kind of membrane costs many times that for a cryogenic plant. In the choice of a more selective but less permeable membrane, the yield will be less but the investment cost will be even higher.

Selected oxygen permeabilities and oxygen/nitrogen selectivity coefficients are given in Table 3. Permeabilities are quite low when the selectivities are at acceptable levels.

It is concluded in a number of studies that practical gas separations can not be performed with conventional membranes in a conventional package. Staging the processes to achieve higher separation never makes sense because that both the energy and membrane area required increase enormously as stages are added.

In order to overcome the permeability-selectivity limitation new approaches are needed. Since membrane technology, especially in gas separation applications, has a great potential and attraction, both scientific and applied researches have been increasing rapidly. Thin-film developing techniques, phase inversion method, coating technology and new packaging techniques have enabled scientist and engineers to produce high selective-high permeable membranes for specific applications. Today most of the studies on gas separation membranes are focused on producing composite structures containing a highly selective skin layer and one or more porous mechanically strong and highly permeable substructures. The active skin layer is generally made up of a highly selective polymeric material while the substructure may be composed of another polymeric material or an inorganic porous material such as alumina, silica etc.

Table 3. Selected oxygen permeabilities and oxygen/nitrogen selectivity coefficients [12].

Polymer	Oxygen Permeability (cc(STP).cm/ sec.cm^2.cmHg.Δp)x 10^9	Oxygen/Nitrogen Selectivity Coefficient
Dimethyl silicone rubber	60	2.2
Natural rubber	2.4	2.7
Ethyl cellulose	2.1	3.1
Polyethylene	0.8	2.8
BPA polycarbonate	0.16	6.7
Butyl rubber	0.14	4.1
Polystyrene	0.12	7.6
Cellulose acetate	0.08	2.5
Methyl cellulose	0.07	2.9
Polyvinyl chloride	0.014	3.0
Nylon 6	0.004	3.8
Mylar	0.0019	6.0
Kel F	0.001	4.3
Polyvinylidene chloride	0.0005	5.0

Chapter IV

POLYMERS

Polymers are defined as large molecules built up by the repetition of small, simple chemical units. This repetition may be linear or branched to form three-dimensional networks. Polymers can exhibit two different states; rubbery and glassy states, depending on the temperature.

Polymers such as natural rubber, silicon rubber and siloxanes are in rubbery state at room temperature, i.e., their glass transition temperature T_g is too low. They show rubber like properties and membranes made up of rubbery polymers show high selectivities and low permeabilities. At sufficiently low temperatures, all amorphous polymers shows the characteristics of glasses including hardness, stiffness, and brittleness. Glassy polymers have low volume coefficient of expansion, a property which is associated with the glassy state. This low coefficient occurs as a result of a change in the slope of the curve of volume versus temperature at the point called *glass-transition temperature*, T_g. Polymers such as polysulfones, polyamides, polyacetates are in glassy state at room temperature so the membranes made up of these materials have glass like properties and have low permeabilities but high selectivities.

4.1 Polysulfones

All commercial polysulfones are linear and although most of them have regular structures they are all amorphous. The high in-chain aromaticity leads to a high T_g value of 190 ^{0}C. Polysulphones are excellent candidates for membrane based gas separation and pervaporation applications because of their chemical and physical properties. A list of physical and chemical properties of polysulfone is given in Table 4. They have been widely used commercially and the first commercial membrane was again polysulphone. Chemical structure of polysulfone can be shown as

$[-C_6H_4\text{-}4\text{-}C(CH_3)_2C_6H_4\text{-}4\text{-}OC_6H_4\text{-}4\text{-}SO_2C_6H_4\text{-}4\text{-}O\text{-}]_n$

Polysulfones are unable to crystallise in spite of their regular structure. It may be expected that the stiff chain with its high T_g and T_m would only crystallise with difficulty but in itself this would not be expected to inhibit it completely. One suggestion is that whereas the ether link has a bond angle of 120^0 the C-S-C bond angle is 105 degrees and that it is difficult to fit these bond angles into a crystal lattice. Although the structure is polar, much of the polarity is frozen-in at normal service temperatures. In such conditions electrical insulation properties are quite good even at high frequencies. In addition to the heat deformation resistance, polysulfones are also resistant to chemical change on heating. This has been explained by the high degree of resonance which gives an enhanced bond strength. Therefore it can stand thermal and ionizing radiation without cross-linking. Since the sulphur is in its highest oxidation state electrons are away from the benzene rings so that the structure does not oxidize easily. The commercial polysulphones are generally resistant to aqueous acids and alkalis although they can not stand to concentrated sulphuric acid. It is not dissolved by aliphatic hydrocarbons but they are soluble in solvents include dimethylformamide and dimethlyacetamide since they have high polarity.

The primary features of the commercial polysulphones are their exceptional resistance to creep, good high temperature resistance, rigidity, transparency and self-extinguishing characteristics. Although these characteristics are also seen in polycarbonates, polysulphones are more heat resistant and have greater resistance to creep while the polycarbonates have a higher tensile impact strength as well as being less expensive. Polysulphones are tough. There are small differences among the main types of polysulphones. For example the polyethersulphones have better creep resistance at high temperatures, e.g. 150 ^{0}C, significantly higher heat distortion temperatures and superior room temperature mechanical properties. Higher molecular weight grades show greater resistance to stress cracking, have better long term strength under load and better impact strength.

Table 4. Properties of polysulfone.

Property	**Value**
Specific Gravity	1.24
Shrinkage,in/in,1/8 in. thick	0.0070
Shrinkage,in/in,1/4 in. thick	0.0080
Water Absorption, % 24hrs	0.220
Impact, Izod, Notched (Ft-Lb/In)	13.00
Impact, Izod, Unnotched (Ft-Lb/In)	60.00
Tensile Strength (Psi)	10,000
Tensile Elongation (%)	75.000
Tensile Modulus (Psi x E+6)	0.36
Flexual Strength (Psi)	15,000
Flexural Modulus (Psi x E+6)	0.39
Compressive Strength (Psi)	14,000
Hardness (Rockwell R)	120.0
Dielectric Strength (V/Mil)	425
Dielectric Constant(@ 1 MC dry)	3.00
Dissipation Factor(@ 1 MC dry)	0.003
Arc Resistance (sec)	122
Volume Resistivity (ohm-cm)10E##	16.0
Heat Deflection Temp 264 psi(F)	345
Heat Deflection Temp 66 psi(F)	358
Flammability	VI
Thermal Expansion (In/In/F)xE-5	3.100
Thermal Conductivity	1.8

4.2 Polymers for Gas Separation

Gas mixtures can be separated by the selective permeation of their components through membranes or thin barriers of various compositions and structures. Graham [13] is the first scientist who demonstrated this process by showing that air can be enriched in O_2 by permeation through *nonporous* polymer membranes (natural rubber films). Graham's studies on gas "effusion" through orifices showed that gas mixtures can be partially separated also by permeation through microporous membranes by virtue of differences in the molecular weights of these gases (Graham's law). Both of these discoveries resulted, well over a century later, in a substantial number of important applications.

The first large-scale use of membranes to separate gases was in the "gas diffusion" process for the separation of uranium isotopes in the Manhattan Project during World War II. This process was first developed in the U.S. in the 1940s and used microporous membranes. The separation of gas mixtures became economically competitive only in the late 1970s. This was made possible by the development of "asymmetric" and "composite" polymer membranes for water desalination by Loeb and Sourirajan in the 1960s and by other scientists [14]. The first large-scale membrane separation plant based on polymer membranes was installed by Monsanto Co. in 1977 for the recovery of H_2 from industrial gas stream.

A very substantial amount of data on the solution, diffusion, and permeation of many gases and vapours in rubbery and glassy polymers is available. The relationships between the chemical structures of polymers and their gas permeability and selectivity are not totally understood. As a result, new polymer structures aimed at increasing gas selectivity or permeability were synthesised largely based on experience and trial-and-error approach. A common view of structure/permeability relationships of polymers is shown in Figure 6.

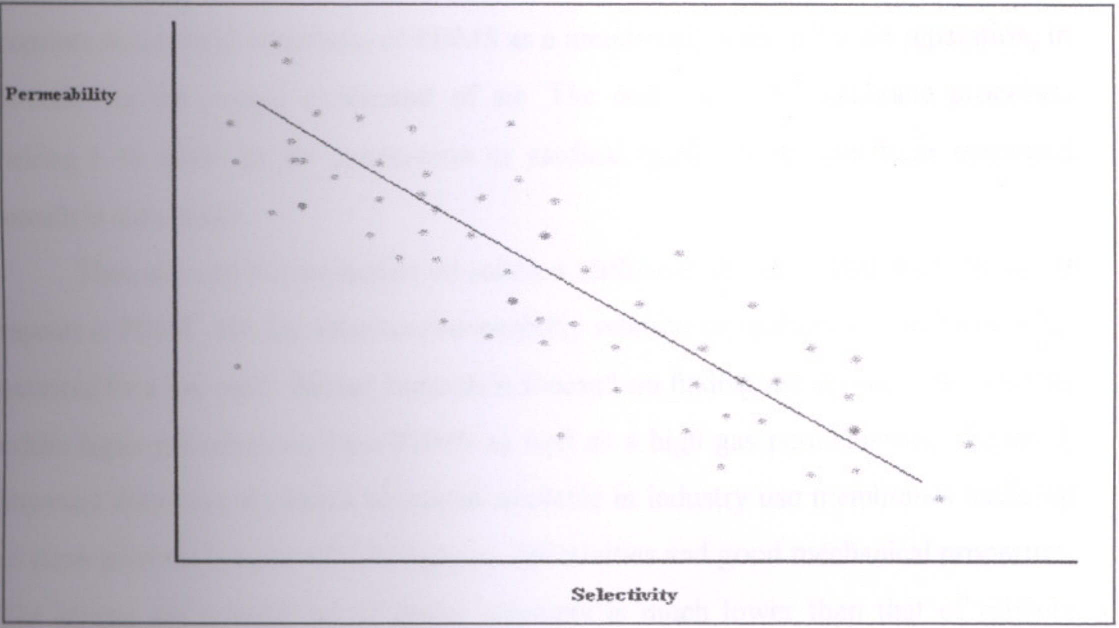

Figure 6. Structure-permeability relation of polymers.

Generally it is possible to comment that,

(1) As the gas permeability of a polymer decreases, its selectivity generally increases. This is the well-known "inverse" permeability/selectivity behaviour which is so often mentioned in the membrane literature.

(2) The polymers that exhibit a high permeability and a low selectivity are in the "rubbery" state at ambient temperature, i.e. their glass transition temperature T_g is lower than the ambient temperature. In contrast, the polymer with a lower permeability but a high selectivity is in the "glassy" state, i.e., its glass transition temperature T_g is above ambient temperature.

Silicone polymers especially polydimethylsiloxane, PDMS, have received considerable attention as membrane materials for gas separation because of their high permeabilities to gases and vapours. In 1957 it has been found that silicone rubber showed much higher gas permeability than all other synthetic polymers known at that time.

The high permeability of PDMS, $[-(CH_3)_2-SiO-]_x$, has been attributed to the large free volume, which may due to the flexibility of the siloxane (-SiO-) linkages of this polymer. Although the gas selectivity of PDMS is very low, many investigators have examined the potential usefulness of PDMS as a membrane material for air separation, in particular for the oxygen enrichment of air. The economics of membrane processes yielding ≥ 30 mol% O_2 for combustion or medical applications have been discussed recently in some detail.

There are well-known studies on solution, diffusion, and permeation of gases and vapours in PDMS. But the structure/permeability relation of rubbery polymers is being examined for a few years. Recent research is focused on finding membrane materials that exhibit higher gas selectivity than PDMS as well as a high gas permeability. Almost all important membrane separation processes available in industry use membranes made up of glassy polymers because of their high gas selectivities and good mechanical properties. The intrinsic gas permeability of glassy polymers is much lower than that of rubbery polymers with few exceptions. But the development of composite and asymmetric membranes from glassy polymers have eliminated this problem. Glassy polymers are characterized by a low intrasegmental mobility and long relaxation times, whereas rubbery polymers exhibit the opposite characteristics. Moreover, the morphology of glassy polymers is viewed as inhomogeneous with respect to the transport of small penetrant molecules, even if the polymers are completely amorphous. For these reasons, the molecular transport mechanisms in glassy polymers are very different from those in rubbery polymers. Thus, the solubility of gases with low critical temperatures (e.g., H_2, He, N_2, CH_4, CO_2) is very low in rubbery polymers, usually within the Henry's law limit at or above ambient temperature. As a result, the gas solubility, diffusion, and permeability coefficients are then are commonly independent of the gas pressure or concentration, provided that the polymers are not significantly plasticized (swelled) by the penetrant gases. By contrast, the solubility, diffusion, and permeability coefficients for such gases in unplasticized glassy polymers are strong functions of the penetrant gas pressure or concentration in the polymers. The above differences in the gas solubility and transport behaviour of rubbery and glassy polymers are due to the fact that the latter polymers are not commonly in a state of true thermodynamic equilibrium. As a result, the structure/permeability relationships of rubbery polymers are quite different from those of glassy polymers.

Chapter V

TRANSPORT MECHANISMS OF GASES IN POLYMERIC MEMBRANES

5.1 Fluxes and Driving Forces in Membrane Separation Processes

Separation in membrane processes is the result of differences in the transport rates of chemical components through the membrane. The transport rate is determined by one or more driving forces acting on components and their mobility and concentration in the membrane. The mobility and concentration of the component in the membrane determine the flux that is produced by the driving force. The mobility is primarily determined by the component's molecular size and physical structure of the membrane material, while the concentration of the component in the interphase is primarily determined by chemical compatibility of the component and the membrane material.

In membrane separation processes there are three main transport types of components through the membrane. The simplest forms is called "passive transport". Here the membrane acts as a physical barrier through which all components are transported under the driving force of a gradient in their electro-chemical potential. Gradients in the electro-chemical potential of a component in the membrane phase may be caused by the differences in pressure, concentration, temperature or electrical potential between the two bulk phases. In the "facilitated transport", the driving force of the transport of the components is again the gradient in their electro-chemical potential in the membrane. But the different components are coupled to a specific carrier in the membrane. Facilitated transport is just a special form of the passive transport, which is highly selective. However, in the "active transport" various components may be transported against the gradient of their electro-chemical potential. The driving force for the transport is provided by a chemical reaction within the membrane. Active transport is usually seen in the membranes of living cells.

The transport process itself is a nonequilibrium process and is conventionally described by a equation that relates the flows to the corresponding driving forces in the form of proportionalities. Fick's law, for example, describes the relation between flow of matter and a concentration gradient. Ohm's law describes the relation between an electrical current and an electrical potential gradient, while Fourier's law describes the relation between heat transport and a temperature gradient.

Table 5. Basic transport equations.

Relationship	**Flux**	**Driving force**
$J = -D\ \Delta c/\Delta x$	Mass	Concentration gradient
$I = \Delta\psi/R_e$	Electricity	Electrical potential gradient
$q = -k\Delta t/\Delta x$	Heat	Temperature gradient

For membrane separation processes, only driving forces that can lead to a significant flux of mass are important. These driving forces are hydrostatic pressure, concentration, and electrical potential differences.

a) A hydrostatic pressure difference between two phases separated by a membrane can lead to a volume flux and to a separation of chemical species when the hydrodynamic permeability of the membrane is different for different components.

b) A concentration difference between two phases are separated by a membrane can lead to a transport of matter and to a separation of various chemical species when the diffusivity and the concentration of various chemical species in the membrane are different for different components.

c) A difference in the electrical potential between two phases separated by a membrane can lead to a transport of matter and to a separation of various chemical species when the different charged particles show different mobilities in the membrane.

5.2 Transport Models

The overall driving force for the transport of a chemical component through a membrane is the gradient in its chemical potential. A net mass flux trough the membrane may not be obtained even in the presence of one or more other gradients.

Although membrane application has its roots up to 1800's, the principle of transport of gases in polymers has not been totally understood. Nowadays much of the research in polymer science and membrane science have been focused on the transport mechanisms of molecules in polymeric structure as well as the development of new promising membrane materials.

Generally models describing the transport of gas molecules in polymeric systems are divided into three main groups: molecular, microscopic and macroscopic models. Molecular models attempt to analyse specific motions of penetrants and polymer chains. The models are based on intermolecular forces and require one or more adjustable parameters, therefore calculations based on molecular models and simulation of transport in glassy polymers take very long computer times. Recent developments in computer capacities more realistic models are available. Microscopic models are derived from free-volume, statistical-mechanical, energy, structure or other considerations, microscopic models provide expressions for gas diffusion coefficients or permeability coefficients or both. Generally they are based on "free-volume" concept in polymers but due to swelling and polymer crystallinity have complications. A well-known microscopic model is "dual-mode" sorption model. But almost all microscopic model have some disadvantages because transport mechanisms in glassy and rubbery polymers are very different. Macroscopic models are based on that gas permeation is a complex process controlled by the diffusion of penetrant gas molecules in the membrane matrix. It assume that the gas dissolved in the membrane and the gas in contact with the interfaces establish an equilibrium at these interfaces. The permeation of gas molecules in nonporous polymeric membranes will be explained with respect to well-known "solution-diffusion" mechanism as well as another famous mechanism called "pore flow" model.

5.3 The Solution-Diffusion Model

The excellent review of Wijmans and Basier [15] is a good source for understanding the solution-diffusion model. Separation of species in a membrane based processes is achieved by the membrane's ability to control the permeation rates of the different species. Two models are used to describe this permeation process. The first is the solution-diffusion model, in which permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. A separation is achieved between different permeants because of differences in the amount of material that dissolves in the membrane and the rate at which the material diffuses through the membrane.

The second is pore-flow model, in which permeants are separated by pressure-driven convective flow through tiny pores. A separation is achieved between different permeants because one of the permeants is filtered from some of the pores in the membrane through which other permeants move. Both models were proposed in the 19.th century, but the pore-flow model was more popular until the mid-1940s. However, during the 1940s, the solution-diffusion model was used to explain transport of gases through polymeric films. Today solution-diffusion model is widely accepted but there still are a few die-hard pore-flow modelers use this models to explain reverse osmosis. By using solution-diffusion model, transport equations can be derived for dialysis, reverse osmosis, gas permeation, and pervaporation.

Overall driving force that produces a net flux of permeants is the gradient in their chemical potential and the other driving forces of pressure, temperature and electromotive forces are interrelated.

Thus the flux is J_i of a component, i,

$$J_i=-L_i\, d\mu_i/dx \qquad (1)$$

where $d\mu/dx$ is the gradient in chemical potential of component i and L_i is a coefficient of proportionality linking the chemical potential driving force with flux. All the common driving forces, like concentration, pressure, temperature, and electromotive gradients, can be reduced to chemical potential gradients. And their effect on flux expressed by this equation. This is very useful, because membrane processes may include more than one driving force. Assuming that only driving forces generated by concentration and pressure gradients exist, the chemical potential can be written as

$$d\mu_i = RT d\ln(\gamma_i c_i) + v_i dp \qquad (2)$$

where c_i is the molar concentration (mol/mol) of component i, γ_i is the activity coefficient linking concentration with activity, p is the pressure, and v_i is the molar volume of component i.

In incompressible phases, such as a liquid or a solid membrane, volume does not change with pressure. Integrating above equation with respect to concentration and pressure gives

$$\mu_i = \mu_i^0 + RT\ln(\gamma_i c_i) + v_i(p - p_i^0) \qquad (3)$$

where μ_i^0 is the chemical potential of pure i at a reference pressure p_i^0.

In compressible gases, the molar volume changes with pressure; using the ideal gas laws in integrating the same equation gives

$$\mu_i = \mu_i^0 + RT\ln(\gamma_i c_i) + RT\ln(p/p_i^0) \qquad (4)$$

To ensure that the reference chemical potential μ_i^0 is identical in those two equations, the reference pressure p_i^0 is defined as the saturation vapor pressure of i, p_i^0. Those equations can then be rewritten as

$$\mu_i = \mu_i^0 + RT\ln(\gamma_i c_i) + v(p - p_{i\,sat}) \qquad (5)$$

for incompressible liquids and the membrane phase and

$$\mu_i = \mu_i^0 + RT\ln(\gamma_i c_i) + RT\ln(p/p_{i\,sat}) \qquad (6)$$

for compressible gases.

All models describing permeation have some assumptions. Usually, the first assumption is that the fluids on both side of the membrane are in equilibrium with the membrane material at the interfaces so there is a continuous gradient in chemical potential from one side of the membrane to the other. This means that the rates of absorption and desorption at the membrane interface are much higher than the rate of diffusion through the membrane. This appears to be valid in all membrane processes, but may fail if there is a chemical reaction like in facilitated transport.

The solution-diffusion and pore-flow models are different in one point: the chemical potential gradient in the membrane,

- the solution-diffusion model assumes that the pressure within a membrane is uniform and the chemical potential gradient across the membrane is expressed only as a concentration gradient.
- the pore-flow model assumes that the concentrations of solvent and solute within a membrane are uniform and the chemical potential gradient across the membrane is expressed only as a pressure gradient.

These two assumptions are illustrated in Figure 6 and Figure 7 which shows pressure-driven permeation of a component by solution-diffusion and by pore-flow. In both models, the differences in pressure across the membrane (p_0-p_l) produces a gradient in chemical potential. In the pore-flow model, the pressure difference produces a smooth gradient in pressure through the membrane, but the solvent activity ($\gamma_i c_i$) remains constant within the membrane. However, the solution-diffusion model assumes that, when a pressure is applied across a dense membrane, the pressure everywhere within the membrane is constant at the high-pressure value. This assumes, in effect, that solution-diffusion membranes transmit pressure in the same way as liquids. Consequently, the pressure difference across the membranes is expressed as a concentration gradient within the membrane.

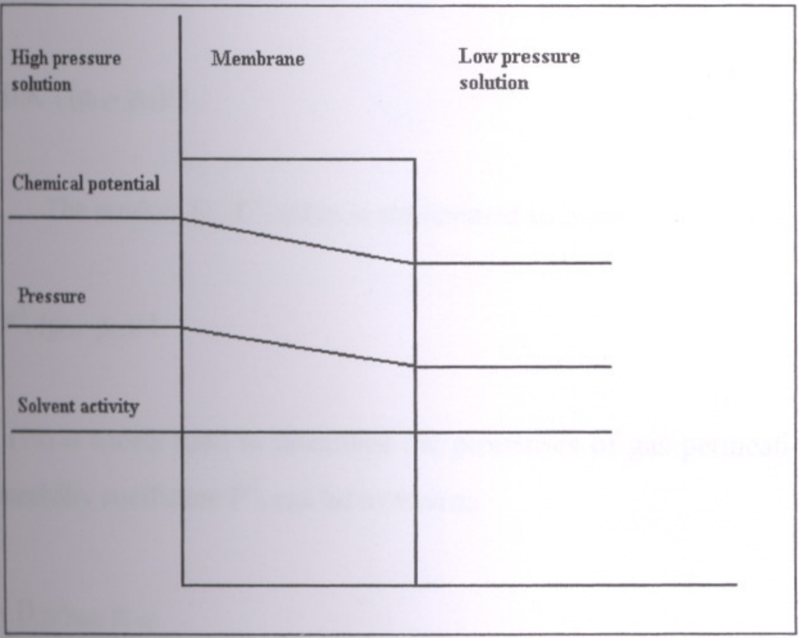

Figure 7. Schematic represantation of pore-flow model [15].

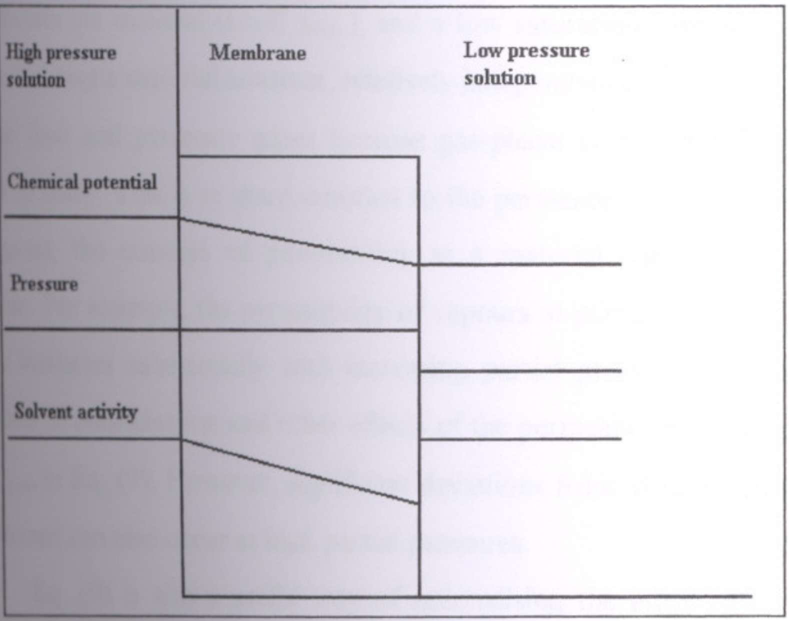

Figure 8. Schematic represantation of solution-diffusion model [15].

Skipping some mathematical expressions and thermodynamic calculations, the flux can be expressed as,

$$J_i = D_i K^G_i \, (p_{i\,o} - p_{i\,l}) / l \tag{7}$$

The product $D_i . K^G_i$ often is abbreviated to a permeability coefficient, P^G_i , thus,

$$J_i = P^G_i \, (p_{i\,o} - p_{i\,l}) / l \tag{8}$$

Eq. (19) is widely used to determine the properties of gas permeation membranes. The permeability coefficient P^G_i can be written as

$$P^G_i = D_i \gamma_i / \gamma_{i(m)} \, p_{i\,sat} \tag{9}$$

Eq. (9) is not a commonly used expression for gas phase membrane permeability, but it shows that large permeability coefficients are obtained for compounds with a large diffusion coefficient (D_i), a limited affinity for the gas phase (high γ_i), a high affinity for the membrane material (small $\gamma_{i(m)}$), and a low saturation vapour pressure ($P_{i,sat}$). P^G_i is close to being a material constant, relatively independent of the composition and pressure of the feed and permeate gases because gas-phase activity coefficients, γ_ii are usually close to unity. This is in sharp contrast to the permeability constant for liquids but even for gases, the concept of permeability as a material constant must be treated with caution. For example, the permeability of vapours at partial pressures close to saturation often increases substantially with increasing partial pressure. This effect is commonly ascribed to plasticisation and other effects of the permeant on the membrane changing D_i and $\gamma_{i(m)}$ in Eq. (9). However, significant deviations from ideality of the vapour's activity coefficient can also occur at high partial pressures.

Eq. (9) is also a useful way of rationalising the effect of molecular weight on permeability. The permeant's saturation vapour pressure $p_{i,sat}$ and diffusion coefficient both decrease with increasing molecular weight creating competing effects on the permeability coefficient. In glassy polymers, the decrease in diffusion coefficient far outweighs other effects, and permeabilities fall significantly as molecular weight increases. In rubbery polymers, on the other hand, the two effects are more balanced. For molecular weights up to 100, permeability generally increases with increasing molecular weight because $p_{i,sat}$ is the dominant term. Above molecular weight 100, the molecular weight term gradually becomes dominant, and permeabilities fall with increasing molecular weight of the permeant. Generally the molecular weight increases from CH_4 to C_5H_{12}, the effect of the decrease in $p_{i,sat}$ is larger than the effect of increasing size or D_i. Above pentane, however, the trend is reversed.

Chapter VI

POLYMERIC MEMBRANE PREPARATION METHODS

Among a number of polymeric membrane preparation techniques, five of them are mostly used for the preparation of polymeric gas separation membranes. These techniques are phase inversion, melt casting, direct polymerization, coating and extrusion.

The polymer is melted and cast on a suitable substrate and further cooled in melt casting techniques. Membranes of polymers that decompose without melting can not be prepared by this technique. Phase inversion technique can be used for these polymers and they are basically solution casting techniques. Melt casting and phase inversion techniques differ considerably in both theory and practice. In phase inversion, polymers are dissolved in suitable solvents and these solutions are cast on substrates. Phase inversion techniques replaced the melt casting techniques and commercial membranes nowadays are prepared mostly by phase inversion techniques.

Polymeric membranes which exhibit high permeabilities and selectivities can be prepared by phase inversion method. In this method polymer is dissolved in a solvent which may be pure solvent or a mixture of solvents and nonsolvents. Generally this solution is cast on a support, i.e., a glass or metal plate and then the polymer is precipitated, and a flat or tubular membrane is obtained. Four different techniques can be distinguished in phase inversion processes [16].

Within the phase inversion process four different techniques can be distinguished:

(a) Precipitation from the vapour phase. Membrane formation is accomplished by the penetration of a precipitant for the polymer into the solution film from the vapour phase saturated with the solvent used. A porous membrane is produced without a skin and with uniform distribution of pores over the membrane thickness. This is one of the oldest phase inversion techniques.

(b) Precipitation by controlled evaporation. The polymer is dissolved in a mixture of a good and a poor solvent, of which the good solvent is more volatile. The polymer precipitates when the solvent mixture shifts in composition during evaporation to a higher nonsolvent content. A skinned membrane can thus be obtained.

(c) Immersion precipitation. This technique, which was first used successfully for the preparation of a reverse osmosis membrane, has been studied and exploited mostly for the production of skinned membranes. The characteristic feature is the immersion of the cast polymer film in a nonsolvent bath. The polymer precipitates asymmetric a result of the solvent loss and nonsolvent penetration.

(d) Thermal precipitation. A solution of the polymer in a mixed solvent is on the verge of precipitation, is brought to separation by a cooling step. When evaporation of the solvent has not been prevented the membrane can have a skin.

Some characteristic features of phase inversion techniques are:

(i) A ternary system. The process involves at least on a polymer component, a solvent and a nonsolvent. The latter two must be miscible.

(ii) Mass transfer. The polymer solution is subject to a transfer of solvent and nonsolvent in such a way that the nonsolvent concentration in the film increases. Mass transfer starts at the interface between the polymer film and the coagulation medium (vapour or liquid). The changes in composition in the film are governed by diffusion. No mass transfer takes place in thermal precipitation without evaporation.

(iii) Precipitation. As a result of the increase of the nonsolvent content the polymer solution becomes thermodynamically unstable and phase separation will occur. So an important aspect of the phase inversion process is associated with the demixing phenomena possible in ternary systems. These phenomena include not only the phase equilibria but also the kinetics of phase separation, as the formation of membranes is a dynamic process.

Precipitation by controlled evaporation can be further accomplished in two different ways: ternary and binary phase inversion methods. In ternary phase inversion the polymer is dissolved in a mixture of good and poor solvent as stated earlier. Precipitation is accomplished by the removal of the good solvent where the poor solvent replaces the good solvent in the membrane structure and further removed by drying. This may cause the formation of an open structure. In binary phase inversion the polymer is dissolved in a good solvent. Precipitation and formation of the polymeric membrane is accomplished by the removal of the solvent. The membranes may be denser than the ternary phase inversion membranes with smaller pore sizes. Both techniques yield skinned membranes with porous substructures. Since phase inversion methods enable more options and freedom during the preparation of membranes and is applicable in laboratory conditions, this method is usually the choice of membrane preparation.

Another approach to produce polymeric membranes is the direct polymerization of the membrane onto a substrate. The polymer film produced on the substrate can then be removed for use or left on the substrate to form a layered composite membrane. These techniques necessitate specific reactors and the development of new control mechanisms to become commercial.

Polymeric membranes can also be produced by coating substrate with a polymeric film which will become the actual membrane. Substrates and the polymeric films are produced separately in this technique. Coated membranes are usually referred as composite membranes since they consist of more then one material (polymer and organic/inorganic support).

Extrusion technique have been mostly used in research laboratories for the preparation of filled and unfilled polymeric membranes but have no commercial applications. In all extrusion techniques, polymers are usually heated under high pressure and forced to flow through a slit. The homogeneous distribution of the filler particles are important in polymer-filler composite membrane extrusion.

Chapter VII

SECOND PHASES IN POLYMER-COMPOSITE MEMBRANES

Much of the research on membrane science and technology have been focused on the development of new membrane preparation techniques and materials that will break the upper bond limitation described in the previous sections. Although there are promising polymer synthesised recently with high permeabilities and selectivities, an alternative way to increase the membrane permeability and selectivity involves the introduction of second phases into the membrane matrix. These materials are generally porous with polar molecules but nonporous materials can also be used. Carbon fillers, molecular sieves and other nonporous materials are mostly introduced as second phases into the polymeric membranes for this purpose.

Active carbons used as carbon fillers are generally considered as hydrophobic materials. The surface properties of the carbonaceous adsorbent play a major role in the adsorption processes. Active carbons are always associated with appreciable amounts of oxygen. The competitive adsorption of polar molecules is greatly influenced by the presence of surface oxygen groups and the removal of oxygen is very important. Active carbons show a selective sorption for the aromatic compounds in a mixture with alcohols, especially in the low concentration range for the aromatic component. The selectivity is higher if the carbonaceous adsorbent is totally outgassed.

Nonporous materials such as zirconia, titania etc, can be used as fillers in polymeric membranes. Addition of these materials may increase the permeability of the membrane since they increase the free volume in the matrix, , but this may also cause a decrease in total selectivity.

Molecular sieves used in polymeric membranes as second phases consist of two important groups. Carbon molecular sieves are produced by thermal decomposition in a controlled chemical and thermal environment of non melting polymeric materials or by the carbonization of coal. The main difference between CMS and active carbon is that the pore size distribution is much narrower and the mean pore size is in the range of molecular dimensions (5-7 A).

Zeolites are crystalline hydrated aluminosilicates of group 1 and group 2 elements such as sodium, potassium, magnesium, calcium, strontium, and barium. Zeolites are 'framework' aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing of all oxygens [17]. Zeolites may be represented by the empirical formula

$$M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$$

In this oxide formula, x is generally equal to or greater than 2 since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, n is the cation valence. The framework contains channels and interconnected voids which are occupied by cations and water molecules. The interconnected microcrystalline voids and channels are responsible for the very specific properties of zeolites. The aperture size is typically in the range of molecular dimensions, i.e. 3 to 10 A. The aluminum atom is trivalent and therefore an excess of negative charge is introduced in the network when Si is replaced by Al in the tetraheda. This charge is compensated by non-framework cations located near the negative charges; the most common ones being Na^+, K^+ and Ca^{++}. The number of cations is thus determined by the number of aluminum atoms in the framework. Because of the presence of cations, these zeolites are polar adsorbents. This means that molecules such as water, ammonia (strong dipoles), carbon dioxide, nitrogen (quadrupolar) and aromatic hydrocarbons (π layer interaction) are adsorbed more strongly than non polar species of comparable molecular weight. Zeolites with a high Si/Al ratio are hydrophobic and adsorption is mainly governed by Van der Waals forces.

Therefore four main factors influence the properties of a zeolite:

1. Pore size which acts on the ability of a molecule to enter and diffuse through the zeolite framework
2. Si/Al ratio which determines the number of cations and thus the hydrophilicity of the zeolite framework

3. Type of cation (valence and sizes).
4. Direction of the pores (1, 2, or 3D porous network).

Some applications of zeolites in the separation of gaseous mixtures are dehydration of industrial gases using hydrophilic zeolites, the separation of air by preferential equilibrium sorption of nitrogen and the removal of H_2S from sour gas.

Zeolites listed in Table 5 are hydrophilic and aluminum rich zeolites. A patent was filed for the synthesis of zeolite ZSM-5 in1972. This zeolite presented a major breakthrough since it was the first hydrophobic zeolite synthesised as such. Other zeolites like mordenite can be made hydrophobic only through leaching out of the framework aluminum. The synthesis of aluminum-poor ZSM-5 and its counter part silicalite resulted in a number of articles that revealed the special properties of these synthetic and hydrophobic zeolites. It was soon recognised that the unique properties of ZSM-5 and silicalite are related to the low aluminum content of these zeolites and the fact that the channels are straight and without constrictions. Steps were taken to synthesise aluminum-free silicalite ($x = \infty$, which to our definition is not a zeolite, but rather a "molecular sieve"). The separation of alcohol-water mixtures with silicalite has received special attention. The synthesis of ZSM-5 and silicalite has lead to new applications for zeolites and zeolite based processes. The latest development in zeolite technology is the synthesis of aluminophosphate based molecular sieves.

Table 6. Types of natural zeolites [5].

Zeolite	Dominant cations	Geological age of host rock	Abundance
Analcime	Na	Quat.-Carbon	Abundant
Chabazite	Na, K, Ca	Quat.-Mio.	Common
Clinoptilolite	Na, K, Ca	Quat.-Carbon	Abundant
Epistilbite	Ca	Miocene	Rare
Erionite	K, Na, Ca	Ouat.-Eoc.	Common
Faujasite	Ca, Na	Ouatenary	Rare
Ferrierite	K, Na, Mg	Miocene	Rare
Garronite	Ca, Na	Miocene	Rare
Gismondine	Ca, Na, K	Ouat.-Carbon	Rare
Gonnardite	Na, Ca	Ouat.-Mio.	Rare
Harmotome	Ba	Neogene	Rare
Heulandite	Ca, Na	Plio.-Carbon	Abundant
Laumontite	Ca	Plio.-Devon	Abundant
Levynite	Ca	Pliocene	Rare
Mesolite	Ca, Na	Neogene	Rare
Mordenite	Na, Ca, K	Ouat.-Carbon	Abundant
Natrolite	Na	Ouat.-Perm.	Common
Phillipsite	K, Na, Ca	Ouat.-Carbon	Abundant
Scolecite	Ca	Mio.-Perm.	Rare
Stilbite	Ca, Na	Ouat.-Jura.	Common
Thomsonite	Ca, Na	Ouat.-Jura.	Common
Wairakite	Ca	Ouat.-Cret.	Common
Yugawaralite	Ca	Miocene	Rare

Chapter VIII

EXPERIMENTAL

8.1 Materials

Polymeric material used in this study was polysulfone purchased from Aldrich Chemical Company. The properties of polysulfone is given in Table 7. Dimethylformamide (DMF) and Dichloromethane (DCM) (Reidel-deHaën) were used as solvents. The properties of these solvents are given in Table 8. Clinoptilolite (a natural zeolite from Gordes, Turkey) and 13X (a synthetic zeolite purchased from Aldrich Chemical Company) were used in this study. The synthetic zeolite has been reported to have an average pore size of 10 A^0 and a particle size of 2 μm by the company.

Table 7. Properties of polysulfone.

Chemical structure	$[-C_6H_4-4-C(CH_3)_2C_6H_4-4-OC_6H_4-4-SO_2C_6H_4-4-O-]_n$
Refractive index, n_D	1.6330
Density (g/cm^3)	1.24
Molecular weight, M_n	22,000

Table 8. Properties of DMF and DCM.

Property	Dimethylformamide, DMF	Dichloromethane, DCM
Chemical structure	C_3H_7NO	CH_2Cl_2
Molecular Weight, g/Mol	73.09	84.93
Density, g/cm^3	0.949	1.33
Purity, min.	99%	99%
Boiling Temperature, C	140	40

8.2 Conditioning of the Zeolites

Since synthetic zeolite 13X was purchased as a powder, it was necessary to run a particle size measurement and determine the average particle size. Although 13X was purchased as 2 μm particles, very hydrophilic zeolite particles may form agglomerates in the presence of moisture causing an increase in the average particle size. Particle size measurement was performed on synthetic zeolite 13X using a Malvern Mastersizer particle size analyzer. The particle size was also determined by optical microscope (Olympus BX 60M) pictures.

Natural zeolite was obtained from Gordes, Turkey in the form of rocks. Since grinding of the natural zeolites is difficult, rocks were soaked in a water bath for a couple of days. These rock were then reduced in size to 1-2 cm in diameter pieces and after drying in air they were ready for ball-milling. Zirconia balls were used as grinding media during ball-milling.

There are four main factors influencing the performance of ball-milling:

1. The percentage of grinding media filling mill volume,
2. The percentage of void space filled by the slurry,
3. The volume percentage of solids in the slurry,
4. Optimum speed of the rotation of the jar

These four parameters were set as 44 vol.%, 39.7 %, 44.4 vol.% and 101rpm respectively. The calculation method used in the determination of these conditions are given Appendix A. The total volume of the jar used was 1260 cc. Ball-milling was carried out for 8 hours and ethanol was used as the grinding vehicle. After ball-milling the slurry was dried and the zeolite powder was obtained. Particles less than 10 μm in diameter were separated according to Stoke's law in a zeolite-water solution. Terminal velocity of a particle in a fluid under gravitational force is:

$$v = (\rho_s - \rho_f)\, g\, d \,/\, 18\, \mu$$

where ρ_s and ρ_f are densities of the solid and the fluid, g is the acceleration of gravity, d is the diameter of the particle and μ is the viscosity of the fluid. For ρ_s=1600 g/cm^3 ρ_f=1000 g/cm^3, g=9,81 m/s^2, the terminal velocity of a 10 μm particle was calculated as ν = 3.27 10^{-5} m/s.

The time required for the particles to settle down could easily be determined using this terminal velocity. For example for a height of 10 cm, the time required for 10 μm particles to settle to the bottom of the container was estimated as 51 minutes. The suspension was then separated from the solids settled to the bottom of the container after a set time of 51 minutes. This suspension was further dried at 80 ^{0}C in an oven for the recovery of fine zeolite particles. In order to get rid of the water adsorbed on the zeolite surface, natural and synthetic zeolites were dried in a vacuum oven at 150 ^{0}C and 0.2 atm. for 4 hours before their use. Polysulfone was used in the experiments without any further treatment.

8.3 Membrane Preparation

In this study four different groups of polymer-zeolite composite membranes were prepared. All of the membranes prepared had a polysulfone matrix with two different zeolites and solvents. The compositions and the codes of the membranes prepared are given in Table 9. In a specific code the first letter indicates the solvent type, the second indicates the zeolite type and the final number stands for the zeolite loading. In the remainder of this thesis these codes will be used.

It is very important to maintain similar conditions such as temperature, pressure in each step of the preparation since the mechanical properties and the performance (i.e. selectivity and permeability) of the polymeric membranes heavily depend on these preparation conditions. Phase inversion technique was used for the preparation of the polymer-zeolite composite membranes.

Four major sets of membranes were prepared in this work (Sets AC, AS, BC and BS). A set is a group of membranes containing the same zeolite type and solvent in their structures but having different zeolite loading. In order to maintain similar properties in all of the solutions the weight of the polysulfone, and the volume of the solvent were kept constant. The weight of the polysulfone, the volume of the solvent and the weight of the zeolite with respect to the zeolite loading for a set are tabulated in Table 9.

Table 9. Membranes with respect to solvent and zeolite types.

Polymer	Solvent	Zeolite	Zeolite Loading (%)	Code
Polysulfone	DCM	Clinoptilolite	20	AC2
Polysulfone	DCM	Clinoptilolite	30	AC3
Polysulfone	DCM	Clinoptilolite	40	AC4
Polysulfone	DCM	Clinoptilolite	50	AC5
Polysulfone	DCM	13X	20	AS2
Polysulfone	DCM	13X	30	AS3
Polysulfone	DCM	13X	40	AS4
Polysulfone	DCM	13X	50	AS5
Polysulfone	DMF	Clinoptilolite	20	BC2
Polysulfone	DMF	Clinoptilolite	30	BC3
Polysulfone	DMF	Clinoptilolite	40	BC4
Polysulfone	DMF	Clinoptilolite	50	BC5
Polysulfone	DMF	13X	20	BS2
Polysulfone	DMF	13X	30	BS3
Polysulfone	DMF	13X	40	BS4
Polysulfone	DMF	13X	50	BS5

Table 10. The weight of the polysulfone and zeolite and the volume of solvent in a set.

Polysulfone (g)	Solvent (cc)	Zeolite (g)	Zeolite loading (%)
5	20	0,55	10
5	20	1,25	20
5	20	2,15	30
5	20	3,30	40
5	20	5,00	50

There are four main steps during the preparation of polymer-zeolite composite membranes by phase inversion method:

1. Preparation of a well-dispersed zeolite suspension in the respective solvent.
2. Dissolution of the polymer in zeolite suspension.
3. Casting of a film of the well-dispersed polymer-zeolite solution.
4. Subsequent solvent removal in air or in an oven at a suitable temperature under vacuum.

During preparation of the polymer-zeolite composite membranes in each set, zeolite was first stirred in the solvent and kept in an ultrasound bath for 15 minutes in order to break up the clusters of particles formed during powder drying. The polymer was then added and the solution was stirred for 24 hours or until a homogeneous dispersion was obtained. These solutions were then cast on a glass plate through a 300 μm slit after air bubbles had been removed. Evaporation of the solvent was carried out under ambient conditions for 6 hours. The resulting membranes were about 60-80 μm thick depending on the solvent and the zeolite used. The flow diagram of the membrane preparation procedure and the picture of the film casting setup are shown in Figure 9 and 10 respectively.

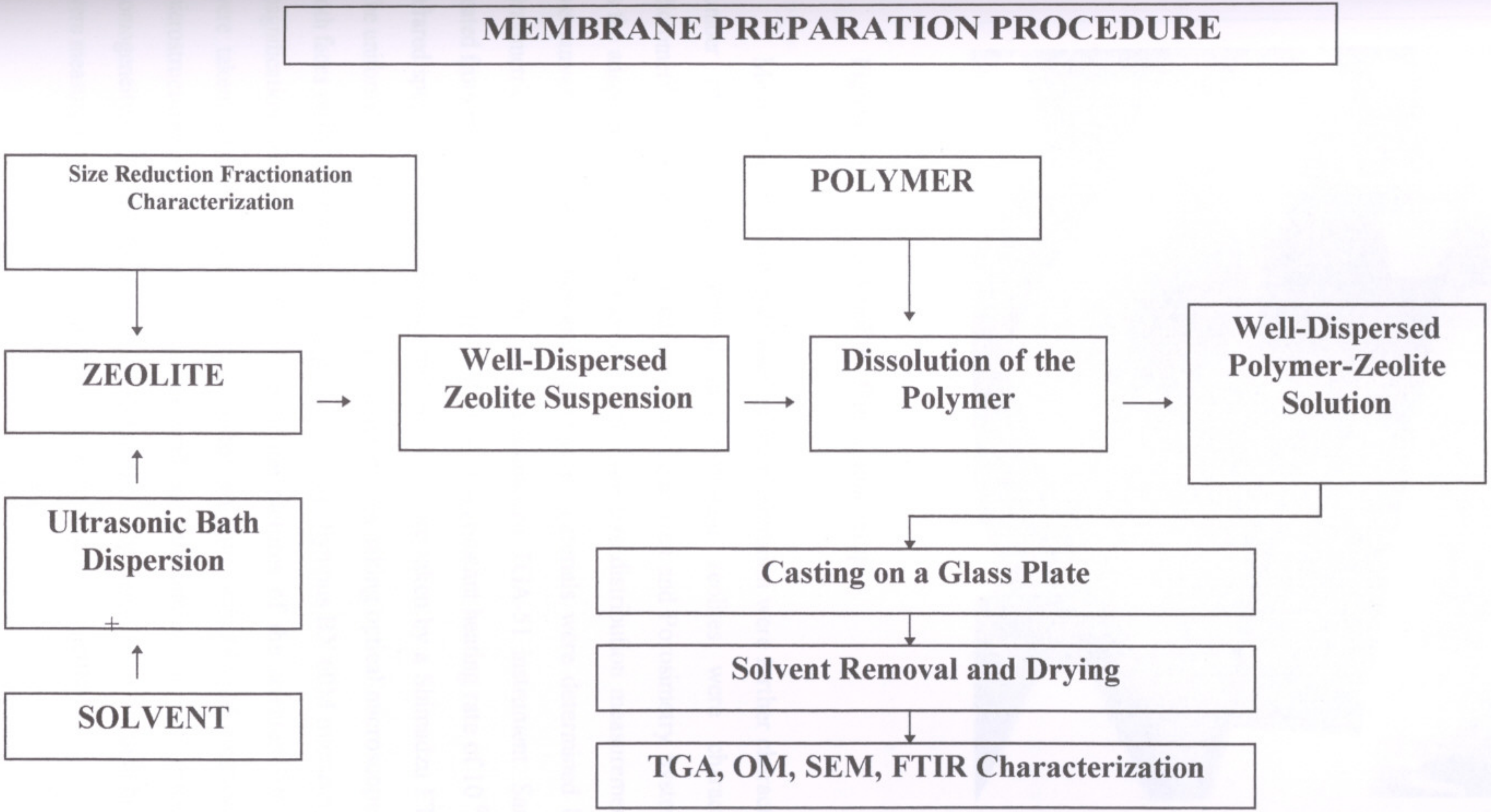

Figure 9. The flow diagram of the membrane preparation procedure.

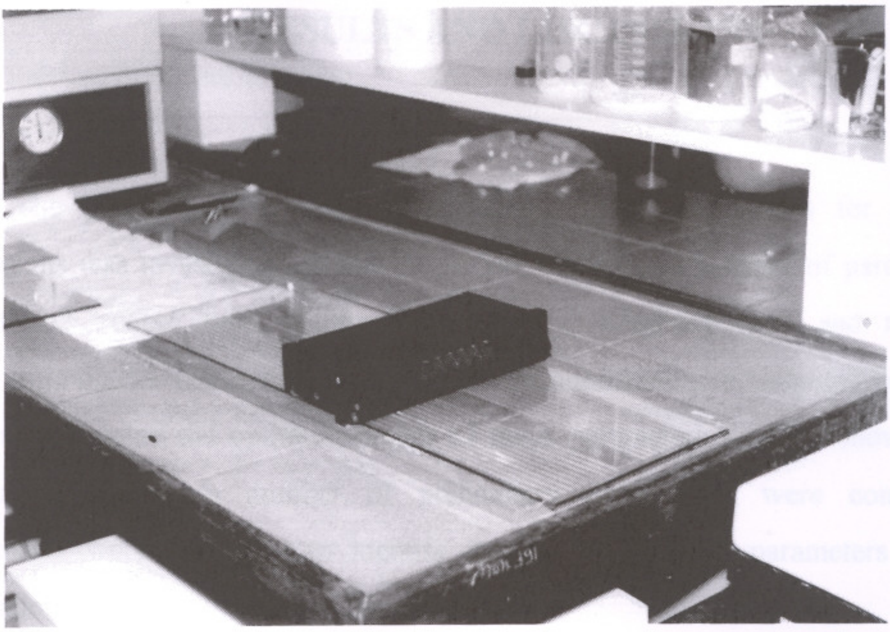

Figure 10. The picture of the film casting setup.

Membranes and materials used in the preparation were further characterized by a number of techniques. Natural and synthetic zeolites were characterized by Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System using N_2 as the adsorptive gas for surface area and pore size distribution measurements. Weight loss curves of all membranes and the starting materials were determined by Thermal Gravimetric Analysis (TGA) by using a Shimadzu TGA-51 instrument. Samples were heated from room temperature to 1000 ^{0}C with a constant heating rate of 10 ^{0}C/min. The infrared spectra of all membranes and zeolites were taken by a Shimadzu FTIR system. The uniformity of the membranes was examined by taking optical microscope pictures of both faces of the membranes by using a reflected Olympus BX 60M microscope at 150X magnification. Scanning electron microscope pictures of the selected AS membranes were taken. These pictures were expected to give valuable information about the microstructure of the membranes as well as information on the distribution and homogeneity of the zeolite particles in the matrix. The densities of the membrane samples were measured by using an Archimedes water displacement method.

Chapter IX

RESULTS AND DISCUSSIONS

The preparation of polymer-zeolite composite membranes for gas separation applications was investigated in this work. The effects of a number of parameters such as solvent and zeolite type, zeolite loading, polymer/solvent ratio and the preparation temperature on the microstructure of the final membrane were investigated in some depth. In order to determine the optimum ranges of these parameters for the following membrane preparation studies, a number of preliminary experiments were conducted. These experiments were necessary to identify the effects of these parameters on membrane preparation.

Optimum polymer/solvent ratios, both for dimethylformamide (DMF) and dichloromethane (DCM), were determined in two sets of preliminary experiments. The visual observations on the properties of the membranes with respect to different polymer/solvent ratios are given in Tables 12 and Table 13. During these experiments other process variables were kept constant. The optimum polymer/solvent ratio was determined as 0.25 and fixed at this value throughout rest of this work

Table 11. Effect of polymer/solvent ratio for polysulfone/DMF system.

Polysulfone / DMF (g/cc)	Final structure
0.10	Large holes, cracks , nonuniform thickness
0.20	Pinholes, small cracks, mechanically strong
0.25	Uniform thickness, no pinholes or defects
0.30	Uniform thickness, no pinholes but cracks
0.40	Large cracks, uniform thickness

Table 12. Effect of polymer/solvent ratio for polysulfone/DCM system.

Polysulfone / DCM (g/cc)	Final structure
0.10	Very thin, nonuniform thickness
0.20	No pinholes or defects but mechanically weak
0.25	No pinholes or defects, mechanically strong
0.30	No pinholes but small cracks
0.40	No pinholes but large cracks

Another set of experiments were carried out in order to determine the maximum zeolite loading possible without defects, cracks or pinholes on the surface of the membrane. PS-DCM-13X and PS-DMF-13X membranes (corresponding to AS and BS series) were prepared with zeolite loading from 10% to 80%. Membranes with 70% and 80% zeolite 13X loadings had problems with the dissolution of the polymer during the preparation of the casting solution. The viscosity of the solution was too high and the solution became almost nonviscous. Although the films with 70 and 80% loadings had no pinholes or defects and had uniform zeolite distribution, large cracks were present in the films. The film area without cracks was too small to be used as membrane. Thus the maximum zeolite loading was set at 50% in order to prevent any solubility problems although 60% loading was still possible.

A maximum zeolite loading of 50% and a polymer/solvent ratio of 0.25 were found to be optimum at the end of these preliminary experiments and the membranes were prepared likewise at room temperature in the rest of the work.

The characterization of the membranes were done by using N_2 adsorption, infrared spectroscopy, thermogravimetric analysis, , optical microscopy and scanning electron microscopy.