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**FORMATION AND CHARACTERIZATION OF MIXED MATRIX COMPOSITE
MATERIALS FOR EFFICIENT ENERGY GAS SEPARATION**

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ABSTRACT

Blend of high performance molecular sieving particles in polymers, known as mixed matrix membrane, offer the potential to combine the excellent gas separation properties of molecular sieving materials with the processability of the polymers (Wahab et al., 2004). The current commercial glassy polymer could provide the commercially acceptable minimum performance of matrix phase compares to rubbery polymer. The objective of this research is to develop a new mixed matrix membrane for O₂/N₂ gas separation. Mixed matrix membrane was prepared in our laboratory to study the effect of incorporating molecular sieve particles into blends of polymers matrix. Blends of Polyethersulfone (PES) and Matrimid[®] 5218 (PI) were prepared by a solution casting method at three different compositions, which are 20/80, 50/50 and 80/20 wt ratio of PI/PES. Zeolite 4A was used as the dispersed particles and its amount was varied between 10% to 50% zeolite loading. Effect of different type of zeolite was also studied using zeolite 3A and 5A. The final membrane was annealed and further dried in vacuum oven at temperature of 150°C to 250°C. The gas separation properties of the membrane were examined using pure gas O₂ and N₂ as the test gases, at room temperature and upstream pressure was varied between 1 atm to 3 atm. The membrane structure was characterized using four different methods which are FTIR, DSC, TGA and SEM. FTIR results showed that some peak shifted and new peaks occurred to the new develop mixed matrix membrane. DSC scanning showed that one T_g is achieved with all the membrane. This confirm that both polymers and zeolite are compatible with each other. TGA analysis showed that by increasing the zeolite loading, it helps to stabilize the thermal degradation of the mixed matrix membrane. Lastly, SEM picture showed that with increasing zeolite loading, it tends to create more voids between the polymer matrix and zeolite surface. These voids create additional path for the gas molecule to pass through instead of observing the molecular sieve effect of the zeolite, thus will increase the gas permeability, while selectivity decrease.

ABSTRAK

Adunan partikel-partikel penapisan molekul yang berprestasi tinggi di dalam polimer, dikenali sebagai membran matrik tercampur, menawarkan potensi untuk menggabungkan bahan-bahan penapisan molekul bagi pemisahan sifat-sifat gas yang istimewa dengan proses kecekapan polimer. Polimer berkaca komersial yang terkini secara komersialnya boleh menyediakan penerimaan prestasi yang minimum pada fasa matrik berbanding polimer bergetah. Objektif kajian ini adalah untuk membangun membran matrik tercampur untuk pemisahan gas O_2/N_2 . Membran matrik tercampur telah disediakan di dalam makmal kami bagi mengkaji kesan penggabungan partikel-partikel penapis molekul ke dalam adunan matrik polimer. Adunan-adunan polietersulfona (PES) dan Matrimid[®] 5218 (PI) telah disediakan menggunakan kaedah penuangan larutan pada tiga komposisi yang berbeza, iaitu 20/80, 50/50 and 80/20 nisbah berat untuk PI/PES. Zeolit 4A telah digunakan sebagai partikel-partikel yang terselerak dan kandungannya telah dipelbagaikan antara 10% sehingga 50% bebanan zeolit. Membran yang terakhir telah dipanas dan selanjutnya dikeringkan di dalam ketuhar vakum pada suhu 150°C sehingga 250°C. Sifat-sifat pemisahan membran telah menggunakan gas O_2 dan N_2 yang asli sebagai gas-gas ujikaji, diuji pada suhu bilik dan tekanan hulu yang dipelbagaikan antara 1 atm sehingga 3 atm. Struktur membran telah dicari menggunakan empat kaedah yang berbeza iaitu FTIR, DSC, TGA dan SEM. Keputusan FTIR menunjukkan sebahagian puncak telah beralih dan puncak yang baru telah terjadi untuk pembangunan matrik tercampur yang baru. Penelitian DSC untuk semua membran telah menunjukkan satu T_g telah dicapai. Ini mengesahkan bahawa kedua-duanya, polimer dan zeolit adalah besesuaian antara satu sama lain. Analisa TGA telah menunjukkan penambahan bebanan zeolit membantu menstabilkan kemerosotan terma membran matrik tercampur. Akhir sekali, gambar SEM juga menunjukkan dengan penambahan bebanan zeolit, ia cenderung untuk membentuk lebih banyak ruang kosong antara matrik polimer dengan permukaan zeolit. Ruangan kosong ini membentuk laluan tambahan untuk molekul gas melaluinya selain daripada pemerhatian kesan penapis

molekul berzeolit, dengan ini akan meningkatkan kebolehtelapan dan sementara itu pemilihan dikurangkan.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Membrane for gas separation has been actively pursued for more than 30 years, while other applications such as dialysis and electro dialysis have been discovered earlier. A membrane is defined as an effective barrier between two phases. A pressure differential is maintained across the membrane under conditions such that at least one of the gases in the feed gas mixture selectively permeates through the membrane from the high-pressure side to the low-pressure side of the membrane (Nawal, 2005). The movement of any species across the membrane is caused by driving forces such as pressure, concentration or electrical potential gradient. Gas mixtures can be separated with porous and with dense membrane. Separation through porous membranes is based on kinetic gas principles whereas dense membrane separation is due to differences in the sorption characteristics and the diffusion rates of the components of a mixture in the membrane (Rautenbach and Albrecht, 1989). The ability of a membrane to control the permeation rate of chemical species through it had made it favorable for separating mixture of gases.

Starting in late 1970's, polymer membranes were developed of sufficient permeability and selectivity to enable their economical industrial use. Polymeric membrane had been used in many applications such as the generation of medium purity nitrogen from compressed air, in the recovery of hydrogen from refinery purge gases and the removal of carbon dioxide from produced natural gas streams. In many cases the polymers employed for the fabrication of the membrane are glassy amorphous materials characterized by high glass transition temperatures, good mechanical strength and an acceptable combination of gas permeability and selectivity properties. Polymeric membrane prepared by using high performance materials such as polyimide, polysulfone and polyethersulfone exhibit high selectivity coefficient and acceptable permeability values separation of gas mixture.

However, polymeric membrane seems to have severe disadvantages that limit its application. The performance of membrane based on polymer material deteriorates with time when used in harsh environment such as high pressure and high temperature. This is due to thermal limitations imposed by module sealing/potting and membrane coating materials. Plasticization which is due to high solubility gases such as CO₂ and H₂S are seriously affecting the surface of polymeric membrane. In 1991, an "upper bound" line which had been identified by Robeson shows the trade-off between selectivity and permeability of existing conventional polymeric membranes. The Robeson's "upper bound" line is shown in Figure 1.1.

Commercial available polymeric membrane lies below the Robeson's "upper bound" line. In fact, previous researchers believe that significant advances in traditional polymeric membrane will be difficult to attain because we are currently approaching the limit of the technology. The trade off between selectivity and permeability is based on traditional structure properties relations of polymeric materials. This upper bound still defines the properties of all truly solution processable polymeric materials today (Mahajan, 2000). This phenomenon had leads for the growing interest in the development of gas separation membranes based on materials that provide better selectivity, thermal stability and chemical stability than those already exist (Saufi, 2002).

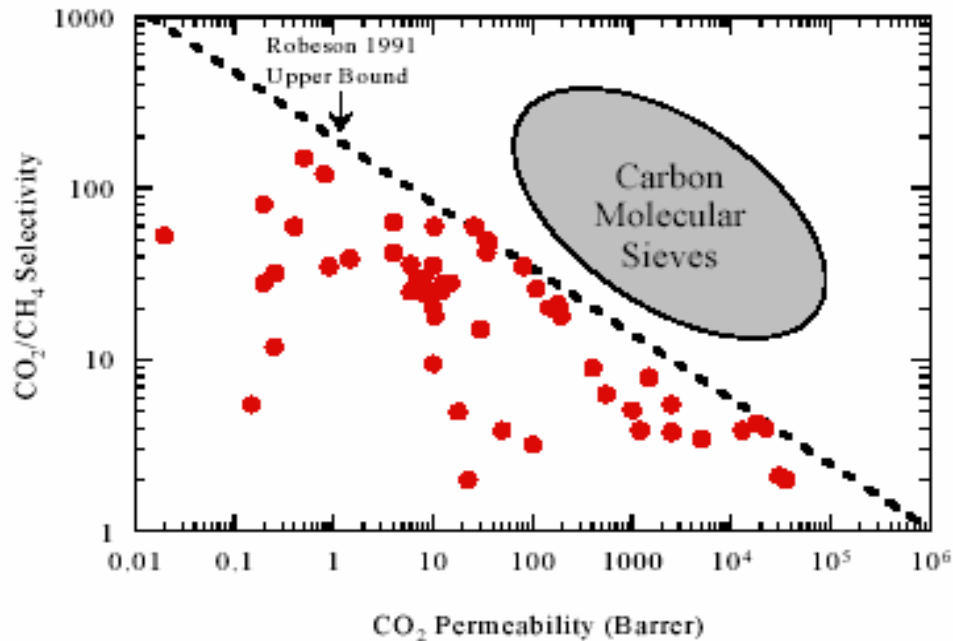


Figure 1.1: Permeation properties of polymeric membrane materials (●) in comparison to the superior properties achievable with molecular sieves materials (shown in shaded region). Shown is the performance trade-off between separation efficiency (CO_2/CH_4 selectivity) productivity (Robeson, 1991).

Note: 1 Barrer = $1 \times 10^{-10} \text{ (cm}^3 \text{ (STP)·cm)/(s·cm}^2\text{·cm Hg)}$.

Inorganic materials such as zeolite, carbon molecular sieve and silica are getting more attention in the recent years in order to seek for a better material that could achieve both high selectivity and permeability. These materials show excellent separation performances for all gases and their separation properties lie well above the Robeson's "upper-bound" line. Other than their superior performance, these materials offer excellent resistance to severe environment (e.g. high pressure), thermally more stable, have well-defined and stable pore structure and good mechanical strength. Despite of all the outstanding advantages of these molecular sieve materials, they are not cost effective and difficult to process as membranes. Therefore, in order to obtain the high performance criteria of molecular sieves and the cost effectiveness of polymer material researches were expanded to develop new type of membrane, which is the mixed matrix membrane.

Mixed matrix membrane is defined as a membrane consists of combination of two or more chemically different materials with a distinct interface between them. The continuous phase is called the matrix. The other main constituent is the reinforcement in the form of fibers or particulates that is, in general, added to the matrix to improve or alter the matrix properties. The interest in developing mixed matrix membrane had started 25 years ago by adding zeolite into polymer matrix. Paul and Kemp (1973) found that addition of zeolite 5A into silicone rubber matrix substantially increased the time lag by, immobilizing adsorption of CO_2 and CH_4 but only slightly affected the steady-state permeation (Zimmerman et al., 1997). Others had extended research on new combination of polymer and molecular sieve, also by introducing new approach to maximize the mixed matrix membrane performance and properties. Figure 1.2 shows the schematics representation of gas flows through polymeric membrane, molecular sieve membrane and mixed matrix membrane.

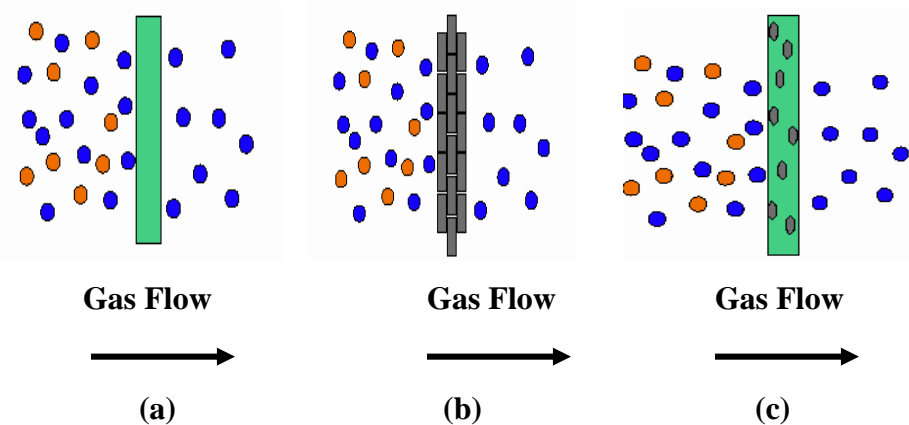


Figure 1.2: Schematic Representations of (a) Polymeric Membrane, (b) Molecular Sieve Membrane (c) Mixed Matrix Membrane (Ismail et al., 2002).

Mixed matrix membrane offer many advantages compared to polymeric membrane alone. This membrane combines the advantages of molecular sieve material and polymer materials such as:

- ✓ Has microporous and nanoporous material adsorption and sieving properties
- ✓ The processability and flexibility of polymer
- ✓ Improvement in resistance to heat, corrosion and chemical degradation.

1.2 Membrane and its Application for O₂/N₂ gas separation

Oxygen is co-produced with nitrogen, argon and other rare gases collectively produced in higher volumes than oxygen. It is recognized as the most important gas and is primarily used in steel manufacturing plants, chemical processing and in water treatment. When purified, oxygen is also used for medical applications. Although oxygen is present in enormous quantities in our breathable air, there exists need of accessing them separately in their gaseous or liquid form. High Purity N₂ is extensively used in food packing, petroleum chemistry and low temperature storage.

Separation of O₂ and N₂ rank as third and fifth bulk chemical produced worldwide (Chem. Eng. News, 1998). High purity O₂ and N₂ are produced by the separation of air through the use of three different unit operations:

1. cryogenic distillation

Essentially a fractional distillation of gaseous mixture by exploiting the difference of relative volatilities of these two components

2. pressure swing sorption (PSA)

This separation process operates as an equilibrium or kinetic process depending on the desire product and adsorbent (Paul and Yampol'skii, 1994)

3. membrane separation

Separation through porous membranes is based on kinetic gas principles whereas dense membrane separation is due to differences in the sorption characteristics and

the diffusion rates of the components of a mixture in the membrane (Rautenbach and Albrecht, 1989)

By the mid-1980s Generon introduced a membrane system to separate nitrogen from air. These first air separation systems were based on poly(4-methyl-1-pentene) membranes with oxygen/nitrogen selectivity of about 4. These membranes were only competitive in a few inch areas requiring 95% nitrogen, but by 1990, Generon, Praxair, and Medall had all produced custom polymers with oxygen/nitrogen selectivities 6-8. Membranes made from these polymers could produce better than 99% nitrogen and offered a cost-competitive alternative to deliver liquid nitrogen for many small users (Baker, 2002)

The majority of both gases are produced by cryogenic distillation of air. Today, the gaseous oxygen market is dominated by cryogenic distillation (99.999% purity) and Pressure Swing Adsorption (95% purity). Current membranes are not capable of economically producing comparable purity, and only a limited number of applications that can utilize low purity (25-50%) O₂ are served by polymeric membranes (Puri, 1996). Oxygen separation using membrane can be attractive in the future if membranes with separation factors 5-6 could be produced (Puri, 1996). For nitrogen, there are many industrial and commercial applications that do not require ultra-high purity, and membranes ideally serve these applications. It is estimated that membranes currently produce 30% of all gaseous nitrogen. Polymeric membranes are dominant in this area and will continue to occupy a strong position in the field; however, as noted above they have stagnated in terms of their transport properties since 1991 (Robeson, 1994). In order to achieve broader penetration and growth (via higher purity or better economics), higher membrane selectivity, combined with equal or greater productivity, is needed (Mahajan, 2002).

1.3 Problem Statement

As energy costs rise, membrane technology for separating gases is likely to play an increasingly important role in reducing the environmental impact and costs of industrial processes. More traditional gas separation processes are shifting to membrane gas separation. Conventional technologies such as the cryogenic distillation of air, condensation to remove condensable organic vapors from gas mixtures, and amine absorption to remove acid gases such as carbon dioxide from natural gas require a gas-to-liquid phase change in the gas mixture that is to be separated. The phase change adds a significant energy cost to the separation cost (Freeman, 2005). Membrane gas separation, on the other hand, does not require a phase change. Thus, it is important to search for new membrane that could achieve superior performance to be able to apply for gas separation. Despite the limitation in achieving both high permeability and selectivity of polymeric membrane, and the limitation of processability of molecular sieves, the novel mixed matrix membrane (MMM) is considered to be the most practical approach to overcome the limitations of both materials.

Early researchers had been done by dispersing molecular sieve particles in rubbery polymer. The first attempt to study mixed matrix membrane was by Paul and Kemp (1973). They used zeolite 5A in silicone rubber and observed delayed diffusional time lag but found no improvement in gas separation properties. Then, Jia et al. (2001) had investigated the effect of incorporating silicalite into silicone rubber. They found that addition of molecular sieves did improve the selectivities of the polymer membrane for O₂/N₂ gas separation.

Gur et al. (1994), prepared a mixed matrix membrane consists of polysulfone matrix embedded with zeolite 13X through a melt extrusion method. He purposely chose large pore zeolite 13X so as to exclude the possibility of separation by size exclusion, hence investigated the possibility of adsorption/desorption kinetics and surface diffusivities of gasses (CO₂, O₂, N₂, CH₄) in the molecular sieve's micropore system. Gur observed no separation improvements and concluded that the role of 13X sieve is

insignificant for this system and the polysulfone matrix governed the separation process. High processability polymer such as Polyimide offer superior combination of selectivity and permeability compared to other conventional polymer available.

Matrimid[®] 5218 which has glass transition temperature of 324.57°C, is one type of Polyimide. This polymer has good processability, has more mobile linkage, allowing for better packing of the polymer and higher selectivities. Incorporating this polymer matrix with molecular sieve such as zeolite could give a better performance for gas separation. Zeolite 4A which have kinetic diameter of 3.8Å, is preferable since it could discriminate easily between gas molecules such as CO₂, CH₄, O₂ and N₂. This is very important since in mixed matrix membrane separation, the molecular sieving phase must be able to discriminate between the molecules of the gas mixture.

Mahajan (2001) had done researched on effects of incorporating Matirimid[®] 5218 with zeolite 4A. Despite of the improvement in performance compared to Polyimide membrane alone, they found that the defects from poor polymer sieve contact causes the mixed matrix membrane to perform well below the predicted values for Matrimid-4A membrane. They concluded that the rigid nature of the polymer causes the polymer chain to delaminate (dewetting) from the sieve as solvent leave the polymer during membrane formation. This problem also had been identified by Vu et al. (2001) in their research.

Since polymer sieve contact is the most important aspect been considered for Mixed Matrix Membrane, it is necessary to develop a membrane for this application, which could achieve good polymer sieve contact, also can stand the harsh process condition besides maintaining the separation performance at elevated pressure condition. It is expected that by blending two different types of polymer for Mixed Matrix Membrane fabrication could improve the contact between polymer matrix and molecular sieve.

1.4 Research Objective

The main objective of this study is to develop a new technique for a mixed matrix membrane formation, which could achieve a better polymer sieve contact and higher gas separation performance. This objective can be further divided into:

1. To select the most compatible combination of polymers and molecular sieve materials formulation for mixed matrix membrane casting that has improvement in the membrane properties.
2. To study the effect zeolite loading to the Mixed Matrix Membrane gas separation performance.
3. To study the effect of blending composition to the mixed matrix membrane gas separation performance.
4. To study the effect of different type of zeolite on the membrane gas separation performance.

1.5 Scope of Research

In order to achieve the objective stated above, the following scopes of works are identified:

- i. Selection for the best polymer combination for blending and molecular sieve materials for mixed matrix membrane formation. A number of commercialized polymers and molecular sieves materials will be study in terms of its chemical and physical properties and its separation properties. These materials should also available at reasonable price.

- ii. Fabricating the mixed matrix membrane in flat sheet form using the selected materials. The procedure for membrane fabrication will follow the methods used by a group of researchers at National University of Singapore (NUS), with some modifications. Parameters that influence the membrane structure and performance will be detail investigated. The membrane will be first fabricated with different zeolite loading in the range of 10% to 50% zeolite loading, at the polymer blending composition. The best zeolite loading will be determined via permeation test. The gas permeation performance will be done using pure gas O₂ and N₂ and evaluating the selectivity for O₂/N₂ by calculation.
- iii. Next, Mixed Matrix Membrane will be fabricated at different polymer blending composition with the best zeolite loading determined earlier. Same performance testing of the membrane will be done for O₂/N₂ gas separation, using pure gas O₂ and N₂. The resultant gas permeation performance will be compared to the performance predicted by Maxwell model.
- iv. The new fabricated membrane will be characterized using several methods such as FTIR, SEM, TGA and DSC. These final characterization will give us a better information of the physical and chemical characteristics of the new developed membrane.

CHAPTER II

LITERATURE REVIEW

2.1 Membrane Gas Separation Technology

2.1.1 History of membrane gas separation

The history of membrane based gas separations can be traced back over 170 years. In 1829 Thomas Graham observed gaseous osmosis for the air-carbon-dioxide system through a wet animal bladder (Kesting and Fritzsche , 1993). Then, J. K. Mitchell in year 1831 observed that balloons made from India rubber put into gas atmospheres of different composition blew up with different velocities, depending on the nature of the gas (Baker, 1991). Mitchell noted that carbon dioxide was absorbed by rubber film to a larger degree than other gases, and he was led to infer, accordingly, that rubber expanded in volume and hence, porosity was induced in the solid sample which provided a way of penetration of CO₂ molecules.

Approximately 25 years later in 1855, Adolph Fick postulated the concept of diffusion and formulated Fick's First Law of diffusion from his studies on gas transport through nitrocellulose membrane (Baker, 1991). Of course, the significance of Fick's

First Law is quite general for many scientific fields, but it is interesting that membranes were the media where it was first established.

Later in 1866, Graham discovered the Graham's law of gas diffusion. Graham's Law describe qualitative about "sorption diffusion" theory for gas transport or permeation through a membrane. In his experiments, gas permeated through the film (natural rubber) into vacuum not into air. Graham established a series of relative permeation rates across the film for a number of gases that is amazing lose to modern estimates of the corresponding properties. He noted that there was no relation between these values and known diffusion coefficients in gases. Therefore, "solution diffusion" mechanism was proposed to describe the mechanism of gas permeate through the rubbery polymer.

Many other important findings in gas permeation research or membrane science more generally, can be attributed to Graham (Graham, 1866). He carried out the first membrane gas separation and obtained oxygen riched air containing 46.6% oxygen. He proposed that increasing the pressure of a gas mixture to be separated should be beneficial for obtaining higher fluxes. He observed that changes in the thickness of films affects the flux but not the composition of permeate gas. He noted the effect of temperature on permeation rates, he prepared the first composite membranes and tried to vary deliberately the chemical nature of the membrane material. The last but not least interesting details are that in the second part of his paper. Graham described his experiments on hydrogen permeation across membranes made of platinum, palladium, and other metals and concluded that they as well as rubber films behaved like non-porous septa.

A quantitative form of this claim was given, probably, by Von Wroblewski who defined what we now call the permeability coefficient as:

$$P = Q \times \frac{l}{\Delta p}$$

where τ is the thickness of the membrane and Δp is the difference between the upstream and downstream pressure. He showed also that the permeability coefficient P can be represented as the product of diffusivity and solubility coefficients, although the units used of the latter differed from those that are in use now. Kayser in 1891 demonstrated the validity of Hendry' law for adsorption of carbon dioxide in natural rubber (Paul and Yampol'skii, 1994). In the twentieth century, more fundamental work was done in the area.

In 1900, Lord Rayleigh measured relative permeabilities of oxygen, nitrogen and argon rubber. Other significant contributions in the understanding of membrane gas transport theory were made by Knudsen in 1908 (Knudsen diffusion defined) and Shakespear in 1917 through 1920 (temperature dependence of gas permeability in membranes studied. Finally, Daynes in 1920 had wrote:” It seems clear that the process of diffusion of a gas through a rubber film is determined by two more less separate processes. Neither of these obeys simple laws. We can hardly expect, therefore, to go very far in our understanding of the problem by studying permeability alone. Measurement must be made simultaneously on the permeability, absorption coefficients, and diffusion-constants, as a minimum, any two of these three quantities” (Daynes, 1920).

This method had been used since until in the 1930s and 1940s, R. M. Barrer widely introduced it to experimental practice, so it is often known as the Dynes-Barrer method. In recognition of the major contribution of barrer to the field of gas permeation, the following definition for the units of the permeability coefficient is widely used:

$$1 \text{ barrer} = 10^{-10} \text{ cm}^3(\text{DTB}).\text{cm}/(\text{cm}^2.\text{s}.\text{cmHg})$$

A great influence on our knowledge of the thermodynamics and diffusion properties of polymers was exerted by the introduction of McBain microbalances (Paul and Yampol'skii, 1994). This simple instrument made it possible to obtain abundant

information, especially for polymer-vapor systems, on solubility coefficients, sorption isotherms, diffusion coefficients, and sorption kinetics.

2.1.2 Gas separation system

There are four principal methods of gas separation which are cryogenics distillation, absorption, adsorption, membrane and separation through reactions.

i. Cryogenics distillation

Cryogenic distillation involves a series of vaporizations and condensations in which the higher boiling species concentrate in the liquid phase which flows down the column and the lower boiling components concentrate in the vapor phase which moves up the column. Heat is removed from the column at the top through a condenser while heat is added at the bottom of the column through the reboiler. Cryogenics is the predominant technology in the separation of atmospheric gases, methane from nitrogen, ethane and ethylene and is also used in hydrogen separations.

ii. Absorption

Absorption is a physical process where a gas is selectively dissolved in a liquid and subsequently recovered through the action of heat, pressure, and/or another chemical. Absorption processes have found major applications in the removal of acid gases such as CO₂ and H₂S (MacLean, 1986). The compensating advantage is that separation can often be effected at a more convenient temperature. Absorption comes into its own when the normal boiling points of the components are widely separated, or where one or more of the components have a strong affinity for a particular solvent. Hence its use with carbon dioxide removal from synthesis gas, and for scrubbing carbon dioxide and sulphur compounds from natural gas.

iii. Adsorption

This technique uses a porous solid material such as a zeolite, an aluminosilicate material, or a carbon molecular sieve to preferentially adsorb one gaseous species versus others. The adsorbent is packed in carbon steel vessels and a higher pressure is used to adsorb while a lower pressure is used to desorb.

iv. Membrane

Membrane which are thin barrier between feed and permeate gas streams have been used to selectively transport fluids since life itself. There have been however, the major technical advances that permit industrial use. The first was the research of Loeb and Sourirajan where thin asymmetric membranes consists of a thin, dense outside layer was formed on a thick, porous base layer, and were developed from cellulose acetate. This allowed high flux as well as good selectivity. This same principle has been applied to many other polymeric systems. Membranes have been formed into separators by either winding flat sheets into spirally wound modules or taking bundles of hollow fibers and casting epoxy resins on both ends and then encasing the bundle in carbon steel shells with appropriate entrance and exit nozzles (MacLean, 1986).

2.1.3 Comparison between gas separation systems

Each of the four gas separation technologies are summarized with respect to their performance, as shown in Table 2.1. Special attention will be given to product quality and general economic considerations.

Table 2.1: Summary for gas separation systems available.

Process	Advantages	Disadvantages
Cryogenic distillation	<ul style="list-style-type: none">• Low power consumption• Could produce high purity products• Could achieve higher recovery compared to other process	<ul style="list-style-type: none">• Unable to economically scale down to very small size• Consist of highly integrated, enclosed system which do not permit easy handling of widely varying feed streams
<ul style="list-style-type: none">• Adsorption	<ul style="list-style-type: none">• Could obtain high purity of products• Can be supplied to remote locations where equipment size is critical	<ul style="list-style-type: none">• Lower recovery of products• Single relatively pure product
<ul style="list-style-type: none">• Absorption	<ul style="list-style-type: none">• Excellent for CO₂ and H₂S removal	<ul style="list-style-type: none">• High partial pressure needed for physical solvents• Low partial pressure needed for chemical solvent slow purity of acid gas
<ul style="list-style-type: none">• Membrane	<ul style="list-style-type: none">• Versatility• Simplicity• Stable at high pressure• Could achieve high purity of product• Could give high recovery• Excellent for separation of hydrogen and hydrocarbon	<ul style="list-style-type: none">• Possible recompression of permeate• Medium purity

2.1.4 Advantages of membrane gas separation

Membrane process is most favorable separating system since it combines several beneficial features that make them attractive for industrial applications. The features are described briefly below:

- i. Separation is on basis of molecular size, which means that the separation process could be carry out at ambient or modest temperature. Thermally sensitive solutes

can be treated without damage. Other environmental stresses, such as imposed by chemical additives and high shear can also be avoided or minimized.

- ii. Membrane separation process did not require any phase change and any latent heat. Thus, it could save lost of energy consumption
- iii. Membrane devices are almost always compact and modular, especially if membrane is provided in a bundle of hollow fibers and spiral wound that occupies high area per unit volume (Spillman and Sherwin, 1990). This factor also leads towards weight and space efficiency, which is important in transportation or offshore platform applications.
- iv. Membrane process is environmental friendly because it produce no waste. In fact, one of the major accomplishments of membrane processes is that they provide a means for recovering value from previously discarded effluents.
- v. Membrane devices could be easily scale up from pilot to commercial size, which allows pilot scale tests with a single module and then direct scale-up by simply using many multiples of this unit.

2.1.5 Polymeric membrane

Polymeric membranes are being increasingly used to effect separations of gas streams in a variety of applications. Examples of such applications would include the generation of medium purity nitrogen from compressed air, the recovery of hydrogen from refinery purged gases and the removal of carbon dioxide from produced natural gas streams. In many cases the polymers employed for the fabrication of the membrane are glassy amorphous materials characterized by high glass transition temperatures, good

mechanical strength and an acceptable combination of gas permeability and selectivity properties.

The permeability of a polymer to gases depends upon both the physical properties of the polymer and the gases concerned. For a particular gas the nature of the polymer and its interaction with the gas will clearly determine the transport behavior. Factors which relate to the molecular structure of the polymer, such as polarity, hydrogen bonding, cohesive energy density, chain flexibility and crystallinity will all have an influence on the transport process (Crank and Park, 1968). It is evident that in correlating gas solubility and diffusivity with polymer structural properties it is difficult to isolate these many inter-relating factors. The selectivity of a polymer to a particular gas mixture is a still more complicated issue, because gases behave competitively in glassy polymer systems.

In developing a clearer understanding of factors affecting glassy polymer gas selectivity, careful studies for pure gas sorption and permeation are required. Analysis of competitive gas sorption and transport behavior should result in the development of a clearer appreciation of the interrelationship between polymer structural factors and gas separation behavior.

2.1.6 Material for polymeric membrane

Any polymeric material will separate gases to some extent. However, proper selection of the polymeric material comprising the membrane is extremely important since it determines the ultimate performance of the gas separation module. In the early period, rubbers and, to a lesser extent, other polymers of natural origin served as the traditional test objects. Studies on rubbers established trends for the effect of the structure, molecular mass and crosslink density of the polymer. The advent of the era of synthetic and semicrystalline polyolefins and other vinylic-type polymers that took place

in the late 1950s and 1960s was accompanied by intense interest for packing applications, where their barrier properties to gases are critical. Gas sorption and diffusion measurements were also widely and effectively used as a probe of polymer structure or morphology.

In the early 1970s interest moved to the glassy state of polymers and, on the other hand, to the direct search for advanced materials for gas separation membranes. The rate of publication, the diversity of polymers investigated, and the number of groups involved in research has increased enormously since the time. Simultaneously, since the 1960s interest in nontraditional types of membrane materials, such as media providing coupled or facilitated transport by means of free or fixed carriers, had emerged.

Membrane processes involve very different processes and hence it might be expected that a number of very different membranes is necessary. The most important membrane qualities to be considered are (Rautenbach and Albrecht, 1989):

- ✓ High selectivity
- ✓ High permeability
- ✓ Mechanical strength
- ✓ Temperature stability
- ✓ Chemical resistance

Table 2.2 listed the membrane processes widely used for separating liquids, gases and organic compounds.

Table 2.2: Summary of available membrane processes

Separation process	Separation mechanism	Feed stream	Typical trans membrane Driving force	Examples of industrial use
Microfiltration	Sieving	Liquid or gas	$\Delta p < 10\text{-}21$ psi	Processing of corn-stillage streams, concentration of emulsions, cell suspension concentration, bacteria and particulate turbidity reduction
Ultrafiltration	Sieving	Liquid	$\Delta p < 50$ psi	Auto-paint recovery, Microemulsion oil recovery, Biomolecule and virus separation from aqueous streams
Dialysis	Sieving and sorption-diffusion	liquid	$\Delta p < 0$ to small Δp sometimes	Hemodialysis primarily
Reverse osmosis	Sorption - diffusion	Liquid	$\Delta p < 0$ often to overcome osmotic pressure, so $\Delta p - \Delta \pi > 0$, usually < 1500 psi	Water desalination, wastewater treatment
Pervaporation	Sorption - diffusion	liquid	Δ (fugacity of i) set by feed liquid mole fraction and permeate vacuum	Dehydration of organic streams and removal of trace organics from aqueous streams
Gas and vapour permeation	Sorption - diffusion	Gas and vapour	Δ (fugacity of i) usually equal to partial pressure difference, Δp_i typically < 1200 psi	Separation of O_2/N_2 , H_2/CH_4 , CO_2/CH_4 , H_2N_2 , H_2/C , O , H_2O/CH_4 , and organic vapours from air

The principle characteristics of these commercialized membrane separation processes can be specified based on the following seven aspects (Kesting, 1985):

- Separation goal
- Nature of species retained (size of the species)
- Nature of species transported through membrane, electrodialysis or volatile
- Minor or major species of the feed solution transported through membrane
- Driving forces
- Mechanism for transport/selectivity
- Phase of feed and permeate streams

2.1.7 Membrane configuration

The membrane and membrane module cannot be considered entirely as two separate entities. Good membrane module designs will in general have the following attributes:

- High are packing density
- Cost-effective manufacturing
- Low pressure drops on the feed and permeate sides
- Good flow distribution and flow pattern
- Minimal concentration polarization

There are six type of membrane module available and used today on a large industrial scale. Each module will be described briefly in this topic. Finally, the performance and processability of each module is summarized in Table 2.3.

i. Plate and frame module

This module often used for ultrafiltration, reverse-osmosis and gas separation. Its design has its origins in the conventional filter press concept. The membranes, porous membrane support plates, and spacers forming the feed flow channel are clamped together and stacked between two end plates (Rautenbach and Albrecht, 1989).

ii. Spiral wound module

Spiral-wound modules were originally used for artificial kidneys, but were fully developed for reverse osmosis system. The wound is placed inside a tubular pressure vessel and feed gas is circulated axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals toward the center and exists via the collection tube.

iii. Capillary membrane module

Capillary membrane module consists of a large number of membrane capillaries with an inner diameter of 0.2 to 3 mm arranged in parallel as a bundle in a shell tube. The feed solution is passed down the center of the membrane capillary and the filtrate, which permeates the capillary wall, is collected in the shell tube.

iv. Hollow fiber module

Hollow fibre has an outer diameter of 50 to 100 μm . In hollow fiber membranes, the selective layer is on the outside of the fibers, which are installed as a bundle of several thousand fibers in a half loop with free ends potted with an epoxy resin in a pressure tube. The feed solution is introduced around the outside of the hollow fibers. The filtrate passes through the fiber walls and flows up the bore to the open end of the fibers at the epoxy head.

v. Tubular membrane module

With this type of module, the membrane is hose form on the inside of pressure tight tubes between 12 and 24mm in diameter. The permeate flows through the wall of the sintered tube to holes arranged at short intervals along the support tube (Rautenbach and Albrecht, 1989).

Table 2.3: Characteristic of major module design (Baker, 1991).

properties	Hollow fibers	Capillary fibers	Spiral - wound	Plate-and-frame	Tubular
Packing density	high	moderate	moderate	low	low
Resistance to fouling	Very poor	good	moderate	good	Very good
Parasitic pressure drops	high	moderate	moderate	moderate	low
High separation process	yes	no	yes	Can be done with difficulty	Can be done with difficulty
Limited to specific types of membrane	yes	yes	no	no	no

2.1.8 Type of membrane

The proper choice of a membrane should be determined by the specific application objective: particulate or dissolved solids removal, hardness reduction or ultra pure water production, removal of specific gases/chemicals etc. There are five main types of membrane often used for separation systems:

- i. Microporous membranes
- ii. Homogeneous dense membranes/ Symmetric membrane
- iii. Asymmetric membranes
- iv. Electrically charged membranes

2.2 Background on mixed matrix membrane

In order to enhance the mechanical properties and separation performance of membrane materials, research efforts are directed to incorporating adsorbents such as zeolites and carbon molecular sieves in polymer matrices. Mixed matrix membrane is not a new concept of membrane. In facts, early researchers have done it by filling rubbery polymer with fillers (resins, activated carbon, zeolite, etc.) and it is used for liquid separation such as reverse osmosis (Solenberger and Withers, 1982), pervaporation, and the separation of submicro particles such as enzymes (Goldberg et al., 1979).

Hennepe et al. (1987) had studies the effect of incorporating silicalite into silicon rubber matrix and tested it for bioreactors fermentation process. He found that there are improvement in alcohol selectivities and permeabilities. Jia et al. (1992) also found that, polydimethylsiloxane (PDMS) matrix filled with silicalite had good results for the ethanol/water pervaporation separation, but showed only slight enhancement for the O₂/N₂ gas separation for the same mixed matrix membranes. There are also research done by using activated carbon as the dispersed material and reported some improvement in the recoveries/removal of VOCs from water to air via pervaporation (Sikdar et al., 2000, Ji and Sikdar, 1996).

For gas separation application, one of the first studies is reported by Paul and Kemp (1973). They investigated the influence of zeolite 5A on the gas permeation (N₂, CO₂, CH₄) and sorption properties of silicon rubber. They found by increasing the zeolite content resulted in an increase in the time needed to reach the steady state conditions due

to their sorption capacity. However, it had only minor effects on the steady state permeation.

Kulprathinpanja et al. (1988) found that membranes composed of silicalite -1 and cellulose acetate have better separating characteristics. The separation factor of O_2/N_2 was increased from 2.99 to 4.06 by increasing the silicalite content from 0 to 25%. Also they have had a considerable improvement for CO_2/N_2 selectivity (a maximum of 9.6) over the unfilled cellulose acetate membranes. Duval et al. (1993) had found that carbon dioxide sorption selective zeolites like silicalite -1, KY and 13X significantly enhanced the separation performances of rubbery polymers. However, zeolite 5A leads to decrease in permeability and unchanged selectivity. This is due to the impermeable character of these particles i.e. carbon dioxide molecules can not diffuse through the porous structure under the conditions applied.

Atalay and Bülbül (1994) have shown that incorporation of some zeolites improved the gas permeation properties of polymeric membranes. The addition of ZSM-5 has increased the gas permeability of silicon rubber membranes. Silicalite-1 filled silicon rubber membranes have showed a relatively higher permeation rate than ZSM-5 for O_2 , N_2 , CO_2 gases. This result emphasizes the role of pore structure of the adsorbent. They also showed that different cation forms of the zeolite additive change the electrostatic interaction in the zeolite channels. Zeolite 4A incorporation into silicon rubber membranes has resulted in considerable decreases in permeabilities of O_2 , N_2 , CO_2 .

They think that this has occurred due to the hydrophilic nature of Zeolite 4A. It has been stated by Paul and Kemp (1973) that if the additive does not have any adsorption/desorption effect then it will act as if it is an inert substance and it will increase the diffusion path but the overall selectivity will remain the same. This indicates that the permeability and selectivity will increase if both the polymer and the additive are selective to the same species. Atalay (1994) also studied the effect of Na-clinoptilolite filling on the separation properties of PDMS membranes, which is the only study in the literature using clinoptilolite. She found that clinoptilolite filling resulted in decrease in

O₂, N₂ and CO₂ permeabilities as the zeolite content increases up to 40 wt%. Selectivities were increased compared to the unfilled membrane.

When clinoptilolite content was increased to 40 wt%, O₂ and CO₂ permeabilities continued to decrease but N₂ permeability started increasing. It has been speculated that the zeolite channels are blocked depending on the cation type, which forces clinoptilolite particles to a N₂ preferred orientation. Table 2.3 below summarized researchers and the types of materials been used for mixed matrix membrane fabrication.

Table 2.4: Previous research on mixed matrix membrane using rubbery polymer

Year	Researchers	Polymer	Mol. sieve	Gas	Ref.
1973	Paul and Kemp	Silicon rubber	Zeolite 5A	CO ₂ /CH ₄	Paul and Kemp, 1973
1991	Jia et al	Silicon rubber	silicalite	O ₂ /N ₂	Jia et al., 1991
1994	Atalay & Bulbul	Silicon rubber	ZSM-5	O ₂ ,N ₂ , CO ₂	Atalay and Bulbül, 1994
1994	Atalay	Polydimethyl siloxane	Na-clinoptilolite	O ₂ ,N ₂ and O ₂	Atalay, 1994
1994	Duval	Polydimethyl siloxane	zeolites like silicalite -1, KY and 13X	O ₂ , CH ₄ , CO ₂ , N ₂	Duval et al., 1993

For glassy polymer matrix filled with molecular sieve, one of the earliest researched is done by Gur (1994) by using zeolite 13A as a filler in polysulfone. He found that no significant effect on the gas permeabilities. Sürer et al. (1994) had used zeolite 4A and 13X as the dispersed materials into polyethersulfone, and found that there is slightly enhancement in the selectivity of O₂/N₂. But, the membrane properties still remain far below the desirable selectivities of current high-performance glassy polymers.

Some other researches using glassy polymer for the continuous phase are summarized in Table 2.4. Next section will explain some of the challenges in mixed matrix membrane formation.

Table 2.5: Previous research on mixed matrix membrane using glassy polymer

Year	Researchers	Polymer	Mol. sieve	Gas	Ref.
1988	Kulprathipanja	Cellulose acetate	silicalite	O ₂ /N ₂	Kulprathipanja, 1988
1994	Suer et al.	Polyether-sulfone	zeolite 4A	O ₂ /N ₂	Suer et al., 1994
1994	Gur	polysulfone	Zeolite 13X	He, O ₂ , CH ₄ , CO ₂ , N ₂	Gur, 1994
2000	Mahajan	Polyvinyl acetate	4A	O ₂ /N ₂	Mahajan, 2002
2001	Reid et al.	Polysulfone	MCM-41 (mesoporous material)	O ₂ , CH ₄ , CO ₂ , N ₂	Reid et al., 2001
2001	Yong et al.	Polyimide (Matrimid 5218)	4A, 5A, 13X, NaY	He, N ₂ , O ₂ , CO ₂ , CH ₄	Yong et al., 2001
2002	Pechar et al.	Polyimide (6FDA-6FpDA-DABA)		He, N ₂ , O ₂ , CO ₂ , CH ₄	Pechar et al., 2002
2002	Mahajan & Koros	Polyimide (Matrimid [®] 5218)	4A+ aminopropyl silane	O ₂ /N ₂	Mahajan & Koros, 2002
2002	Mahajan & Koros	a) Various Polyimide b) PEI (Ultem [®])	4A	O ₂ /N ₂	Mahajan & Koros, 2002
2003	Vu	Polyimide (Matrimid [®] 5218 Ultem [®] 1000)	CMS	O ₂ /N ₂ and CO ₂ /CH ₄ Mixture CO ₂ /CH ₄	Vu, 2001
2003	Vu et al.	Polyimide (Matrimid [®] 5218)	CMS	CO ₂ /CH ₄ with Toluene	Vu et al., 2003
2003	Kurdi & Tremblay	Polyimide (Ultem [®] 1000)	Metallic complexes	Air	Kurdi & Tremblay, 2003
2003	Chung et al.	Polyimide (Matrimid [®] 5218)	Fullerene (C ₆₀)	He, O ₂ , CH ₄ , CO ₂ , N ₂	Chung et al., 2003
2003	Hacarlioglu et al.	Polycarbonate	Polypyrrole powder	N ₂ , O ₂ , CH ₄ , CO ₂ , H ₂ , Ar	Hacarlioglu et al., 2003

2.3 Material selection for mixed matrix membrane

To fabricate a mixed matrix membrane, material selection for polymer matrix as well as sieving material is the key aspect in order to have a membrane with good chemical strength and excellent separation performance. Molecular sieve membranes, namely zeolite and carbon molecular sieve (CMS), feature extremely attractive permeation performance beyond the Robeson's upper bound trade-off limit, to be applied for CO₂/CH₄ gas separation. The molecular sieve must be in between the kinetic diameter of these two molecules. Zeolite 4A, which has an effective aperture size of 3.8Å poses the right type of molecular sieve for this application.

Polymer matrix selection determines minimum membrane performance while molecular sieve addition can only improve membrane selectivity in the absence of defects (Mahajan, 2002). The early researches in mixed matrix membrane employed highly permeable rubbery polymers as polymer matrix embedded with hydrophobic zeolite fillers for the pervaporation separation (Hacarlioglu et al., 2003). Good polymer-sieve contact was due to the soft and flexible structure of rubbery polymer. However, previous research had showed that minimum or no benefit is achieved from incorporation of the sieve phase into a highly permeable rubbery polymer as the majority of the gas diffusion would occur through the lower resistance polymer phase, by passing the sieves.

Glassy polymer that currently dominates gas separation membrane exhibits economically acceptable permeability and selectivity, hence a likely candidate for a successful polymer matrix. Most of current researches in mixed matrix membrane have focused on using glassy polymer as the continuous phase. Although formation of mixed matrix membrane using rigid glassy polymer as continuous phase is more difficult due to poor polymer-sieve contact, some successes were achieved using various techniques to modify the preparation and formation protocol of the glassy polymer-sieve mixed matrix membrane. Otherwise, poor contact will introduce a lower resistance path for leakages to occur, hence reduces selectivity and increases permeability. Polymer such as Matrimid[®] 5218 is an ideal candidate to be used with zeolite 4A since the polymer exhibits

economically acceptable properties and the CO₂ permeability of the polymer is reasonably close to the sieve.

In addition to material selection, research in mixed matrix membrane also covers membrane formation technique, characterization, performance evaluation and modeling. Membrane formation includes the solution preparation, surface treatment, casting process and post treatment. Characterization and performance evaluation are important for better understanding of the relationship between membrane morphology and its transport properties.

2.3.1 Polyimide and derivatives

Polyimides are high temperature engineering polymers originally developed by the DuPont Company. When compared to most other organic or polymeric materials, polyimides exhibit an exceptional combination of thermal stability (>500°C), mechanical toughness and chemical resistance. In addition, they have excellent dielectric properties. Polyimides are rigid with high-melting point, high-transition temperature (T_g), thermally stable polymers formed by the condensation reactions of dianhydrides with diamines, as shown in Figure 2.5. Polyimide such as Matrimid[®] 5218 and Polyetherimide had been used widely as material for gas separation membrane. This polymer exhibits high separation performance for various gases.

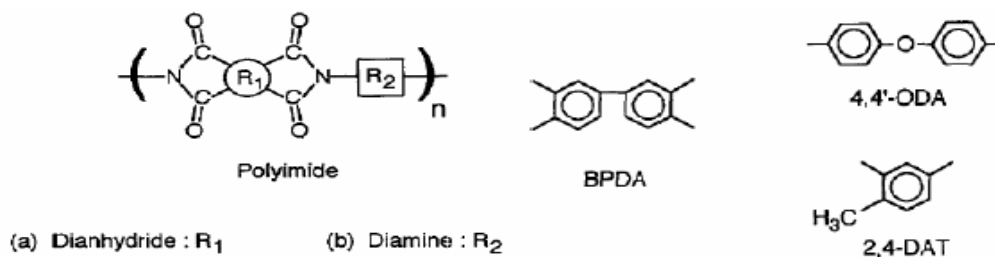


Figure 2.5: Molecular structure of Polyimide (Saufi, 2002)

2.3.2 Molecular sieves

Any material that can exclude molecular species by size can be considered as molecular sieve. J. W. McBain (1932) had other specific explanation which is, molecular sieves is material that exhibit the property of acting as sieves on molecular scale. Basically, molecular sieve materials have uniform pores with diameters in either the micro ($< 2\text{nm}$) or meso ($2\text{-}20\text{nm}$) size range. Among the most popular molecular sieve material that commercially available are zeolite and carbon molecular sieve. Others are glasses, oxides and clay. Molecular sieve materials could give high selectivities (as shown in Figure 1.1) because these materials offer distinctive pore dimensions approaching the molecular dimensions of gases (Vu, 2001). Molecular sieve membrane are rigid, could withstand harsh environment (high temperature and high pressure) and have higher resistance to plasticization.

However, this material had a few disadvantages which limit its application despite of it superior performance. The fabrication of the membranes is not cost effective. Nevertheless, they are fragile, difficult to process and brittle. In fact in many cases it is difficult to obtain even a small area to measure the transport properties of these materials and indirect methods must be used to estimate transport properties (Mahajan, 2000). Therefore, it is a need to develop a membrane which could minimize the cost of using this excellent membrane, by incorporating this material into polymer.

2.3.2 Zeolite

Molecular-sieve zeolites of the most important aluminosilicate variety can be represented by the chemical formula $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$, where y is 2 or greater, M is the charge balancing cation, such as sodium, potassium, magnesium and calcium, n is the cation valence, and w represents the moles of water contained in the zeolitic voids. Zeolite framework is made up of SiO_4 tetrahedra linked together by sharing of oxygen

ions. Substitution of Al for Si generates a charge imbalance, necessitating the inclusion of a cation. The structure contains channels or interconnected voids that are occupied by the cations and water molecules. The water may be removed reversibly, generally by application of heat, which leaves intact the crystalline host structure permeated with micropores that may account for >50% of the micro crystal's volume. Figure 2.6 shows the unit cell structure for zeolite 4A.

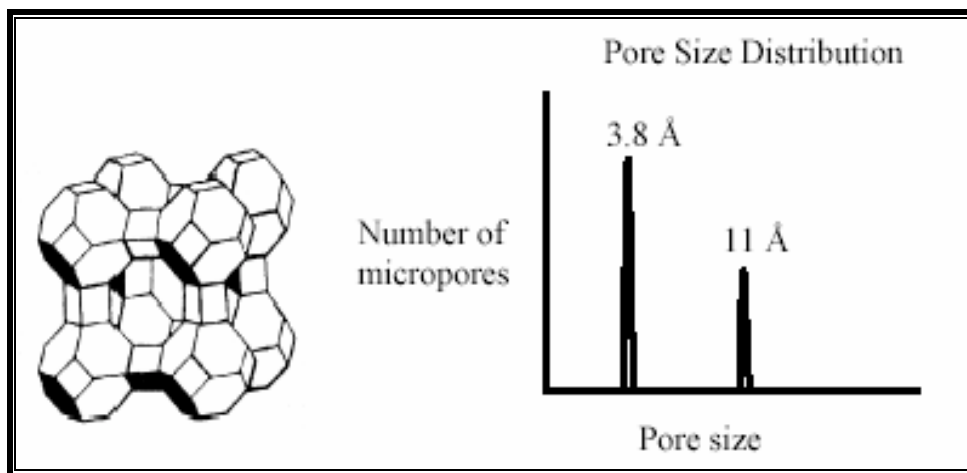


Figure 2.6: Unit cell structure of zeolite 4A. A silicon or aluminum atom is located at each vertex and an oxygen atom at or near the center of each line. For zeolite 4A, the micropore distribution is bimodal, showing the 3.8 Å pore constrictions and 11 Å cavities (Vu, 2001).

Zeolite molecular sieves have special characteristics: the microporous character with uniform pore dimensions, allowing certain hydrocarbon molecules to enter the crystals while rejecting others based on too large a molecular size, the ion-exchange properties which performing all sorts of ion-exchange reactions, and the ability to develop internal acidity which makes the zeolites materials for catalyzing organic reactions and the high thermal stability of the zeolites.

Zeolite molecular sieves have pores of uniform size that are determined by the crystal structure of the material, These pores will completely exclude molecules that are

larger than their diameter, The molecular sieve for a particular separation can thus be selected based on the pore size and the dimensions of the penetrants. Table 2.5 listed some common zeolite molecular-sieve nominal pore aperture as well as gases that are admitted and rejected by this sieves. Table 2.6 is given the Lennard-Jones kinetic diameters of various gas molecules.

Table 2.6: Common zeolite molecular-sieve nominal pore aperture as well as gases that are admitted and rejected by the sieves (Yang, 1987).

Zeolite	Nominal Pore Aperture (Å)	Molecules Admitted	Molecules Excluded
Zeolite 3A	3 Å	H ₂ O, NH ₃ , H ₂ , He, Ne (Molecules with an effective diameter less than 3 Å)	CO ₂ , etc. (Larger than 3 Å)
Zeolite 4A	3.8 Å	CO ₂ , Ar, O ₂ , N ₂ , CO, CH ₄ (Molecules with an effective diameter less than 3.8 Å)	C ₃ H ₈ , etc. (Larger than 3.8 Å)
Zeolite 5A	4.9 Å	C ₃ H ₈ , n-C ₄ H ₁₀ , CF ₂ Cl ₂ , other n-paraffins, n-olefins (Molecules with an effective diameter less than 4.9 Å)	Iso-paraffins, etc. (Larger than 4.9 Å)
Zeolite 10X	8 Å	Iso-paraffins, Iso-olefins, Benzene, Toluene (Molecules with an effective diameter less than 8 Å)	Di-n-butylamine, etc. (Larger than 8 Å)
Zeolite 13X	10 Å	Di-n-butylamine, 1,3,5-Tri ethyl benzene (Molecules with effective diameter less than 10 Å)	(C ₄ F ₉) ₃ -N, etc (Larger than 10 Å)

Table 2.7: Lennard Jones kinetic diameters of various gas molecules (Breck, 1974)

Gas	Kinetic Diameter [Å]
He	2.60
H ₂	2.89
CO ₂	3.30
CH ₄	3.80
O ₂	3.46
N ₂	3.64
CO	3.76

There are four main areas in which zeolites are applied:

- i. Adsorbents/desiccants/separation processes
- ii. Catalyst
- iii. Detergents
- iv. Miscellaneous

2.3.4 Carbon molecular sieve

Carbon molecular sieves (CMS) are nano- and microporous materials that have distributions of pore sizes and interconnected channels that enable fast transport of gas molecules (Kärger and Ruthven, 1992). Within the distribution of pore sizes are constricted, ultramicroporous pore openings with dimensions that are of the same order of magnitude as molecular sizes of gas molecules. As a consequence, the porous nature of carbon molecular sieves allows for high gas permeabilities, yet their molecular sieving morphology permits precise discrimination of gas penetrants to yield highly selective membranes. As expected, permeation through CMS membranes is accomplished by adsorption of gas molecules and activated transport through the selective pore openings

(Koresh and Soffer, 1995). These selective pore constrictions can be visualized as a distribution within the CMS membrane of narrow selective channels connecting open cavities. This view is similar to the structural framework of zeolites, but CMS materials are amorphous (not crystalline) and do not have long-range order of pore constrictions. A conceptual visualization of CMS structure is shown in Figure 2.7, showing constrictions in well-packed regions that allow for molecular sieving (ultramicropores) and the larger sorptive cavities (micropores).

The pore size distribution is consistent with the view that ultramicropores perform the molecular sieving (size-selective) process in carbon molecular sieve materials, while larger micropores connecting ultramicropores provide sorption cavities and allow for high fluxes of gas penetrants by promoting larger average diffusional jumps. This visualization is analogous to that given for zeolites, but the pore size distribution is broader for the amorphous CMS materials unlike the crystalline nature of zeolites. However, CMS membranes offer many advantages over zeolites, most importantly, having the ability to form homogeneous, defect-free membranes for use in gas separation applications. There is a significant body of research work in the literature with CMS membranes within the past two decades.

2.4 Gas transport in polymer and molecular sieving materials

Separation of gases through membrane is the result of differences in the transport rate of chemical species through the membrane interphase. The transport rate is determined by the driving force of forces acting on the individual components and their mobility and concentration within the interphase. The mobility and concentration of the gas mixture within the interphase will determine how large a flux is produced by a given driving force. These driving forces are hydrostatic pressure, concentration difference and electrical potential difference. For a given driving force, the flux through a unit of membrane area is always inversely proportional to the thickness of the selective barrier.

2.4.1 Permeation

Gas mixtures can be separated by porous and non-porous membranes. Membrane performance can be characterized by two main parameters, which are the flux of the gas through membrane (permeability) and the separation efficiency of the membrane (selectivity). The permeabilities of different components in membrane depend on the mechanism by which the components are transported.

A gas mixture of A and B is separate by membrane and the transport flux of penetrant A can be expressed as a quantity called the permeability, P_A , and it is determined by the equation below:

$$P_A = \frac{N_A \cdot \lambda}{\Delta f_A} \quad (\text{Barrer}) \quad (1)$$

where N_A is the molar flux of penetrant A, ℓ is the thickness of the thin selective layer of the membrane and Δf_A is the driving force (partial pressure) of penetrant A across the membrane. Permeability is often expressed in Barrer, where Barrer is:

$$1 \text{ Barrer} = 1 \times 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \text{cmHg}}$$

For asymmetric membrane, the thickness of the thin selective layer is hardly determined. Therefore, the equation becomes:

$$\frac{P_A}{\lambda} = \frac{N_A}{\Delta f_A} \quad (2)$$

where $\frac{P_A}{\lambda}$ is defined as the permeance. Permeance is often expressed in Gas Permeation

Units (GPU)², where GPU is:

$$1 \text{ GPU} = 1 \times 10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{s.cm}^2.\text{cmHg}}$$

In membrane separation process, the thin selective layer act as a barrier that permits a faster permeation rate for one component while rejected another component. The efficiency of the membrane in separating the two components can be expressed as the separation factor:

$$y_{A/B} = \frac{y_A/y_B}{x_A/x_B} \quad (3)$$

where y_A , y_B is the mole fraction of the component in permeate stream and x_A , x_B is the mole fraction of the component in feed stream. If the permeate pressure is under vacuum, the quantity measured is called the ideal separation factors and the expression is:

$$\alpha^*_{A/B} = \frac{P_A}{P_B} \quad (4)$$

The separation factor is the true, practical measured of the actual gas separation for a membrane separation process.

Generally, gas transport through polymeric membrane, and also through molecular sieving materials is modeled by sorption-diffusion mechanism. This mechanism is so named because transport occur when gas molecules from upstream gas phase first sorb into the membrane, then diffuse across it and finally desorb on the downstream gas phase side (Mahajan, 2000). In this mechanism, the permeability of penetrant A is a product of the average diffusion coefficient, $\overline{D_A}$, and the average solubility coefficient, $\overline{S_A}$. This quantity could be expressed by Fick's First Law:

$$N_A = -D_A \frac{dC_A}{dx} \quad (5)$$

$$P_A = \frac{N_A \bullet \lambda}{\Delta f_A} = -D_A \frac{dC_A}{dx} \bullet \frac{\lambda}{\Delta f_A} \quad (6)$$

where dC_A is the concentration gradient between the selective membrane. The equation above can be integrated with the following boundary conditions: $C_A=C_{A,2}$ at $x=0$ (upstream face of membrane) and $C=0$ at $x=\ell$ (downstream face of membrane):

$$\int_0^\lambda \frac{P_A}{\lambda} dx = \int_0^{C_{A,2}} D_A \frac{dD_A}{\Delta f_A} \quad (7)$$

$$P_A = \int_0^{C_{A,2}} \frac{D_A(C_A) dC_A}{C_{A,2}} \frac{C_{A,2}}{f_{A,2}} \quad (8)$$

The right-hand side is simplified with the introduction of the mean diffusion coefficient, $\overline{D_A}$, and the mean sorption coefficient, $\overline{S_A}$:

$$\overline{D_A} = \frac{\int_0^{C_{A,2}} D_A(C_A) dC_A}{\int_0^{C_{A,2}} dC_A} = \frac{\int_0^{C_{A,2}} D_A(C_A) dC_A}{C_{A,2}} \quad (9)$$

$$\overline{S_A} = \frac{\int_0^{C_{A,2}} dC_A}{\int_0^{f_{A,2}} df_A} = \frac{C_{A,2}}{f_{A,2}} \quad (10)$$

Substituting the relationships in equation (9) and (10) into equation (8), the permeability of penetrant A is shown to have a kinetic contribution ($\overline{D_A}$) and a thermodynamic contribution ($\overline{S_A}$):

$$P_A = \overline{D_A} \bullet \overline{S_A} \quad (11)$$

By using the equation above, the permselectivity of penetrant A over penetrant B can also be expressed in terms of their respective mean diffusion coefficients and mean sorption coefficients:

$$\alpha_{A/B}^* = \frac{P_A}{P_B} = \left(\frac{\overline{D_A}}{\overline{D_B}} \right) \left(\frac{\overline{S_A}}{\overline{S_B}} \right) \quad (12)$$

In order to increase the permselectivity of the membrane, it is required to adjust the diffusivity and the solubility of the penetrants. The solubility selectivity is dependent on the relative condensability of gas penetrants and penetrant-membrane medium interactions, whereas diffusivity selectivity is dependent on the relative differences of the diffusion coefficients of gas penetrants through the membrane material (Vu, 2001).

2.4.2 Sorption

The sorption coefficient describes the amount (or concentration) of gas that is taken up by a membrane material at a given pressure or fugacity at equilibrium (Vu, 2001). Sorption of gases through rubbery polymer follows Henry's Law at low concentration, while for higher concentration, more complex explanation is needed. For glassy polymer, this quantity is modeled by the dual-mode sorption model.

For molecular sieving material, Langmuir isotherm (1918) is used instead of other models. According to Langmuir Isotherm, the materials are rigid, thus can only accommodate molecules within certain fixed sites and reach a saturation limit corresponding to a monolayer coverage. The rate of sorption is proportional to the product of the concentration of the penetrant in the gas phase and the amount of available sorption sites, and it reaches a dynamic equilibrium with the desorption rates (Yang, 1987).

2.4.3 Diffusion

Diffusion coefficient is defined as a quantity that measures the mobility of the penetrant molecules in the membrane. For polymers, the diffusion rate is affected by the penetrant size, the packing and mobility of polymer chains, and the cohesive energy of the polymer (Crank and Park, 1968). The diffusion of gas through polymer occurs when the polymer provides an opening for the sorbed penetrant to move into, with the subsequent collapse of the sorbed cage that was previously occupied by the penetrant. This opening results from the thermally induced motion of the polymer segment. Thus, the rate of gas diffusion depends on the concentration of the opening that is adequately large to accept the diffusing molecules (Mahajan, 2000).

For gas separation, diffusion is a function of both the difference in diffusive jump lengths between the penetrants and the frequency of sufficiently-sized gaps. The size and frequency of these gaps differ for differently sized penetrants because of the different gap sizes necessary for a penetrant to execute a diffusive jump. As shown in figure 2.7, the diffusive jumps of gas penetrant in polymer can only occur when gaps of sufficient size are available, whereas diffusion of gas penetrants in molecular sieves occurs through fixed pores of determinate size (Vu, 2001).

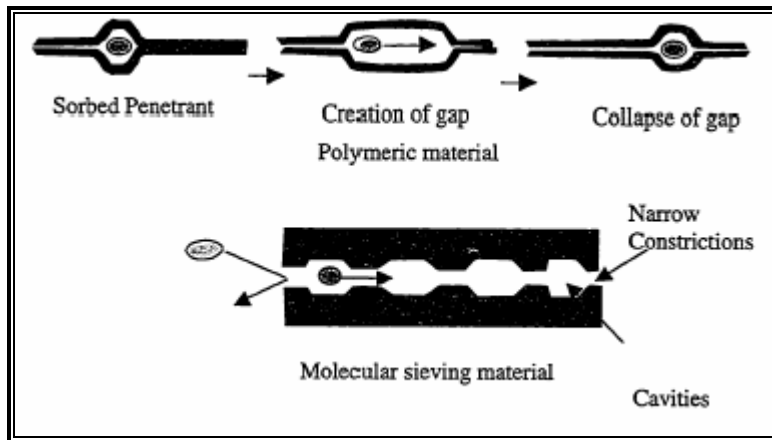


Figure 2.7: Transport of penetrant through polymer and molecular sieves (Mahajan, 2000).

Separation of gases through molecular sieving materials depends on the differences in molecular size of the gases. The diffusion process is envisioned to occur when a gas molecules makes a diffusive jump from one sorption cavity to another through a narrow pore opening. Because large sorption cavities connect these narrow pores in a rigid network structure, high permeabilities can also be realized through this molecular sieving process. In this activated process, the barrier to diffusion is due to the repulsive forces between the gas penetrant and the constricted pores (Kärger and Ruthven, 1992).

Molecular sieve can almost achieve an infinite selectivity for certain gas pairs, if the size difference is such that one of the penetrants can enter the narrow constriction and the other cannot (Mahajan, 2000). It is believed that a more subtle contribution to selectivity is made by entropic factors in molecular sieving materials. This selectivity is called entropic selectivity. This selectivity results from the molecular sieving materials ability, to limit more degrees of rotational freedom for one penetrant compared to another (Crank and Park, 1968).

The diffusion process in these materials is an activated process, thus, the temperature dependence of the diffusion coefficient, D_A , is described by the Arrhenius relationship (Singh, 1997):

$$D_A = D_o \exp\left[-\frac{E_D^{\pm}}{RT}\right] \quad (11)$$

where D_o is the pre-exponential factor, E_D^{\pm} is the activation energy diffusion (positive), R is the universal gas constant and T is the absolute temperature. In rigid molecular sieving materials, penetrant size and pore size are the primary factors influencing the rate of diffusion (Crank and Park, 1968).

The thermodynamics sorption coefficient decreases with temperature according to Van't Hoff's equation (Crank and Park, 1968):

$$S_A = S_O \exp\left[\frac{-H_s}{RT}\right] \quad (12)$$

where S_O is the pre-exponential factor and H_s is the apparent heat of sorption of the penetrant (negative). For gas mixtures, sorption selectivity depends primarily on the condensability of the two penetrants.

The increase in temperature had a better effect on diffusion coefficient than sorption coefficient. This result in an crease in permeability with increasing temperature:

$$P_A = P_O \exp\left[\frac{-E_p}{RT}\right] \quad (13)$$

where

$$P_O = D_O S_O$$

$$E_p = E_D^\pm + H_s$$

2.4.4 Model for performance prediction of mixed matrix membrane

Several theoretical models have been used to predict the permeation properties of mixed matrix membranes as functions of the permeabilities of the continuous and dispersed phases. Petropoulos (1985) presents a comparative summary of various models. A particularly useful model was developed by James C. Maxwell (1873) in 1873 to predict the permittivity of a dielectric. The constitutive equations governing electrical potential and the flux through membranes are analogues, permitting the applicability of Maxwell's results to transport in mixed matrix membranes (Bouma et al., 1997). The solution to calculate the effective permeability of mixed matrix membrane with a dilute dispersion of ellipsoids is (Bouma et al., 1997) :

$$P_{eff} = P_C \left[\frac{n \cdot P_d + (1-n)P_C - (1-n)\phi_d(P_C - P_d)}{n \cdot P_d + (1-n)P_C + n\phi_d(P_C - P_d)} \right] \quad (1)$$

where

P_{eff} = effective permeability of a gas penetrant in the mixed matrix membrane

ϕ_d, ϕ_c = volume fraction of dispersed phase and continuous polymer matrix phase

P_c, P_d = gas penetrant permeabilities in continuous and dispersed phase

N = the shape factor of the dispersed phase

The limit of $0 = n$ corresponds to parallel transport through a mixed matrix membrane made of side-by-side layers of the two phases (laminar) or an arithmetic mean of the dispersed and continuous phase permeabilities:

$$P_{eff} = P_c(1 - \phi) + \phi_d P_d \quad (2)$$

The limit of $1 = n$ corresponds to transport through the two phases (or laminar) in series:

$$P_{eff} = \frac{P_c P_d}{P_d(1 - \phi_d) + \phi_d P_c} \quad (3)$$

The result for dilute suspension of spherical particles ($n=1/3$) is known as the Maxwell equation:

$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \right] \quad (4)$$

Petropoulos has demonstrated that Maxwell Model may be further applicable at higher concentrations. However, Bouma et al. (1997) advises that the Maxwell equation should only be applicable for low loadings because of the assumption that the streamlines around particles are not affected by the presence of nearby particles. Bouma et al. recommends the so-called Bruggeman Model (Banhegyi, 1986) which incorporates an

integration technique to approximate the effect of adding additional particles to a dilute suspension. The Bruggeman equation for a random dispersion of spherical particles is:

$$\left[\frac{(P_{eff}/P_c) - (P_d/P_c)}{1 - (P_d/P_c)} \right] \left(\frac{P_{eff}}{P_c} \right)^{-1/3} = 1 - \phi_d \quad (5)$$

Bouma et al. show that the Bruggeman Model and the Maxwell Model give fairly identical results up to $\phi_d = 0.20$ after which the presence of nearby particles may affect flow patterns, which according to the Bruggeman Model, the Maxwell Model does not account for. After calculating the effective permeabilities of the penetrants through the mixed matrix membrane, the predicted ideal selectivity of the mixed matrix membrane for a gas pair is simply the ratio of effective permeabilities of two competing gas penetrants (Vu, 2001). For example, the ideal selectivity for a mixture consisting of penetrants *A* and *B* is:

$$\alpha_{A/B}^* = \frac{(P_{eff})_A}{(P_{eff})_B} \quad (6)$$

This study will consider the Maxwell and Bruggeman Models for comparisons with the experimental permeation data of mixed matrix films, since both models have been used previously for mixed matrix work and can provide quantitative trends to guide our expected membrane improvements and enhancements with the mixed matrix concept.

2.5 Challenges with mixed matrix film formation

Three types of primary problems had been identified in mixed matrix membrane formation. Vu (2001) had identified these problems as:

1. Surface patterns effects

This problem is due to rapid evaporation of the solvent and temperature gradients in the wet film. With rapid evaporation, surface tension-driven forces from convective flow cells that result in uneven clustering of the molecular sieves articles and the appearance of irregular patterns on the surface.

2. Sedimentation/aggregation

This had led to aggregation with nearby sieve particles due to the low viscosity of mixed matrix membrane slurry solution.

3. Poor polymer-sieve contact

This problem arise from the poor adhesion between the polymer and molecular sieve materials.

Vu had also modified the fabricated membrane in order to minimize these problems. Some of the suggested modifications are:

- i. Sonication of the slurry solution and forming more viscous mixed matrix slurries can reduces the sedimentation and aggregation problems
- ii. Priming/ sizing the molecular sieves with a small quantitiy of polymer or using sizing agent. This modification technique is believed to help in compatibilizing the sieves and the matrix polymer for improved adhesion and also minimized aggregation at high sieves loadings
- iii. By reducing the evaporation rate, which will reduce the surface pattern effects

The proper contact between polymer matrix with the molecular sieve phase is an important aspects in determining the performance of a mixed matrix membrane.

Vankelecom et al. had identified this problem and found that it is due to the high chain

rigidity of glassy polymer (polyimides, polysulfone, etc), therefore their “close packing is disturbed in the vicinity of the zeolite particles”, resulting in voids in the mixed matrix membrane. He modified his membrane by adding silane coupling agent to improve the adhesion between the polymer-sieve interface. The silane agent will formed a covalent bonds between the sieve and polymer. Although there are improvements in the polymer-sieve contact, no improvement in selectivity of the membrane (Duval et al., 1994). Berry et al. (2000) also investigated the effect of using crosslinking (thermal and UV curing) techniques with two silanes on zeolites 3A and 13X. He reported that some evidence of bonding with the silane gel matrix from infrared spectroscopy.

However, Mahajan and Koros (Mahajan and Koros, 2002, Mahajan et al., 1999) had identified some key issues that should be considered to minimize this problem. They made a conclusion that the selection for the polymer matrix phase is very important. The polymer matrix phase must have sufficient permeability for gas molecules to have continuous pathways through the sieves. Choosing a sieve with dimensions capable of discriminating gas penetrants is also an important aspect.

2.6 Contact Between Polymer Matrix Phase and Molecular Sieve Phase

Molecular sieve incorporated into polymer matrix had been studied earlier for rubbery polymer. Researcher had reported that there are improvements for the properties for gas separation membrane. Duval et al. (1993) had reported that for A type zeolites, this method is totally ineffective in improving the permselectivity of the rubbery polymers. This behavior was attributed to the slow diffusion of the sorbed molecules from zeolite to polymer phase.

Glassy polymer embedded with molecular sieve particle had got attention and had first been studied by Suer et. al (1994) for polyethersulfone embedded with zeolite 13X and 4A. They identified that this method had improved the selectivity and permeability of

the membrane with higher zeolite loading. Duval et al. (1994) focused on the formation of interfacial voids due to the poor adhesion of the glassy polymer and the zeolite surface. When silicalite-1 was added into glassy polymers such as cellulose acetate (CA), polysulfone (PSF), polyetherimide (PEI) and polyimide (PI), permeabilities increased but selectivities decreased or maintained. They concluded this result is due to void formation between the polymer phase and molecular sieve phase. Figure 2.8 shows the different between good polymer-sieve contact and poor polymer-sieve contact in membrane structure. One of the method to reduce this poor contact is by adding silane agent. Yong et al. (2001) had added 2, 4, 6-triaminopyrimidine (TAP) to the dope solution before casting the membrane. They found that TAP enhanced the contact of zeolite particles with polyimide chains presumably by forming hydrogen bonding between them. Heat treatment on the membrane film can also help to enhanced the contact between polymer and molecular sieve, besides adding silane agent to the dope solution.

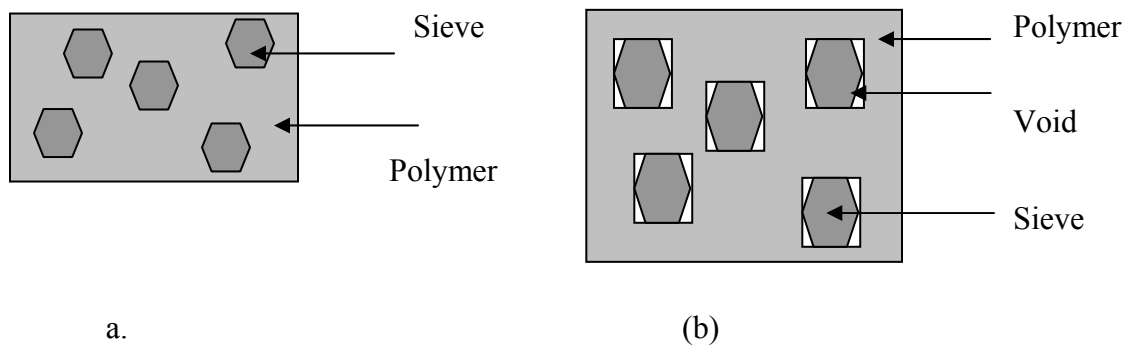


Figure 2.8: Mixed matrix membrane (a) Good polymer-sieve contact (b) poor polymer-sieve contact

2.7 Particle size of MMM

It is known that the permeability of a gas through a zeolite filled polymeric membrane depends on the intrinsic properties of the zeolite and the polymer, the interaction between the two and the percentage of zeolite loading in the mixed matrix membrane (Zimmerman et al., 1997). Birguil et al. (2000) had studied the effect of zeolite particle size on the performance of mixed matrix membrane. In his studies, he chose to use zeolite silicalite as the dispersed phase and PDMS as the polymer matrix. Different sizes of silicalite in the range of 0.1 to 8 μm have been used. Membranes with two different zeolite loadings, which are 20% and 40%, were prepared. He observed that at a same zeolite loading, as the particle size increases, the permeability values of all gases increase quite linearly with the particle size, as shown in Figure 2.9.

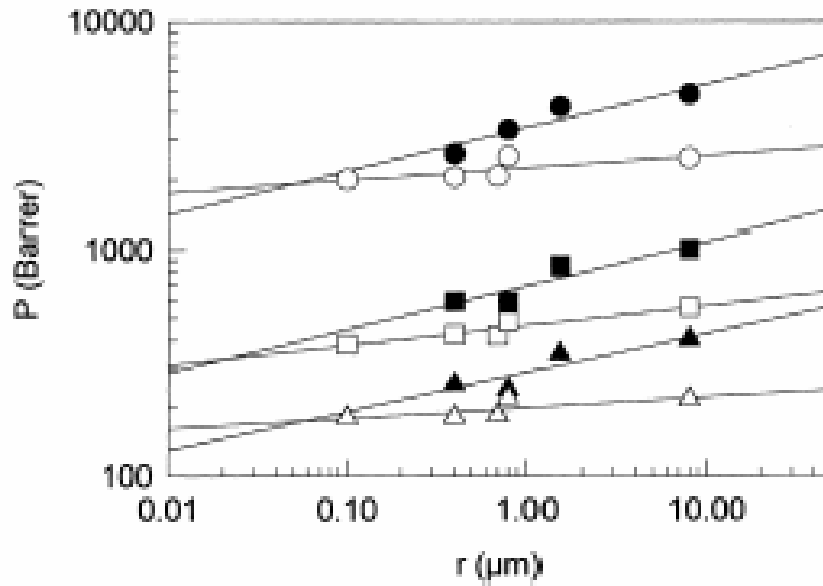


Figure 2.9: Effect of zeolite particle size on the permeabilities of (●) CO₂ 40%, (○) CO₂ 20%, (■) O₂ 40%, (□) O₂ 20%, (▲) N₂ 40%, (△) N₂ 20%. (Birguil et al., 2000).

According to Birguil et al. (2000), this is because when small particle size is used, the zeolites particles in the membranes will attain very large numbers, in which case the

relatively higher number of particles in the sample may lead to additional possible disadvantages. The decreased permeability value with smaller particles sizes are due to the enhanced area and number of zeolite-polymer interfaces that gas molecules have to cross in these cases. If such an effect did exist, however, the permeability values would increase with a decrease in the particle size, exhibiting just the opposite tendency that was observed in Figure 2.9. It was also observed that the effect of zeolite loading seem to be more significant than those of the changes made in the particle size.

From Figure 2.10, it could be noted that the increase on both particle size and loading didn't have a significant effect on the selectivities of the gas separation. At lower particle size, the selectivities seem to increase with increasing zeolite loading. But as the particle size were further increase, the selectivities seems to decrease. He reported that, this results is due to the existence of an optimum zeolite particle size providing a maximum selectivity value for the cases mentioned or maybe due to experimental errors. Birguil had made a conclusion that permeability values increased with respect to the PDMS membrane only when relatively higher zeolite loadings and larger particles sizes are employed in the mixed matrix membrane.

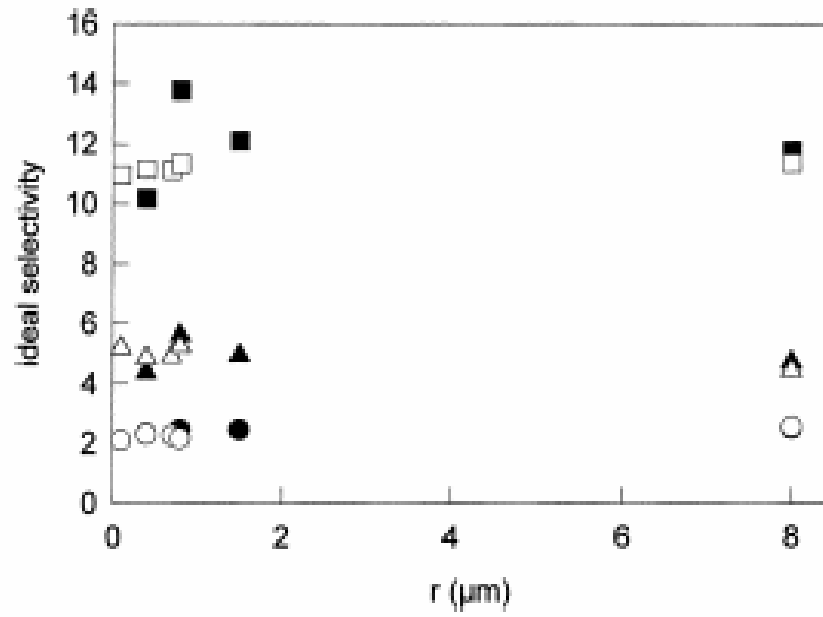


Figure 2.10: Effect of particle size on the (■)CO₂/N₂ 40wt%, (□) CO₂/N₂ 20wt%, (▲) CO₂/O₂ 40wt%, (△) CO₂/O₂ 20wt%, (●)O₂/N₂ 40wt% and (○) O₂/N₂ 20wt% .(Birguil et al., 2000).

CHAPTER III

METHODOLOGY

3.1 Research Design

The challenges faced by polymeric membrane as well as molecular sieves membrane had leads to the development of mixed matrix membrane. This chapter covers the type of materials used to fabricate the mixed matrix membrane as well as the experimental procedures and methods used to test this new membrane. Basically, there are three main steps involve in mixed matrix membrane formation. They are (1) selection of most compatible polymer and sieve material for membrane fabrication, (2) preparation of the polymer-sieve slurry and (3) casting the polymer-sieve mixture to form a mixed matrix membrane film. The selection of suitable membrane material also plays an important role in achieving the best performance in membrane separation process. Figure 3.1 shows the propose research design for this study.

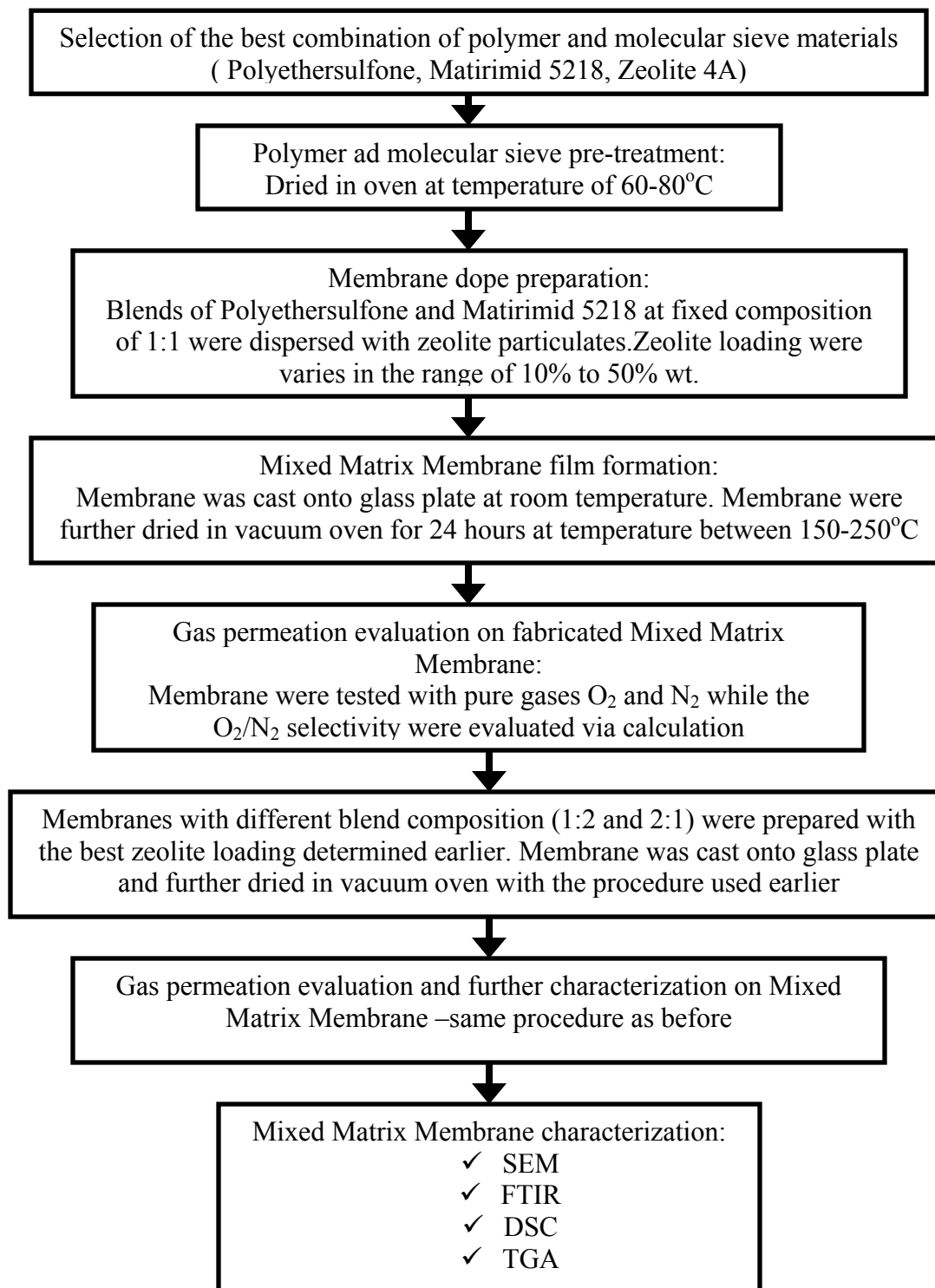


Figure 3.1: Research Design Flowchart

3.2 Material Selection

In mixed matrix membrane formation, selection of suitable polymer matrix, molecular sieve and solvent is an important aspect. This section will discuss about the selection of these three materials and the attractive criteria that had been fulfilled by this three materials.

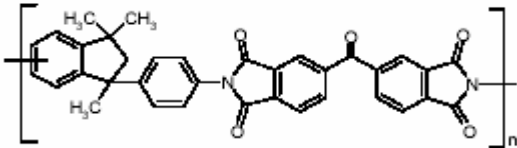
3.2.1 Polymer selection

3.2.1.1 Matrimid®5218

Matrimid®5218 which is supplied by Ciba was selected as the polymer matrix for this study. This polymer is classified as a type of polyimide. Polyimides are rigid, has high T_g , thermally stable polymers formed by the condensation reaction of dianhydrides with diamines (Allcock and Lampe, 1990). Matrimid® 5218 is formed from two monomers: 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-diamino-1,1'-biphenyl-2,2'-dicarbonyl chloride (DAPI) (Vu, 2001). It has more mobile linkages, allowing for better packing of the polymer and higher selectivities (Vu, 2001).

Both polymers are soluble in several common organic solvents, such as dichloromethane (CH_2Cl_2) and 1-methyl-2-pyrrolidone (NMP) and can be prepared as films from solution casting or as hollow fibers from spinning. Table 3.1 listed the properties for Matrimid®5218.

Table 3.1: Chemical and physical properties of Matrimid[®] 5218 (Vu, 2001).

Properties	
Chemical structure	 <p>3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 5(6)-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane (DAPI)</p>
Density (g/cm ³)	1.24
Glass transition temperature, T _g	320°C

3.2.1.2 Polyethersulfone

Radel A Polyethersulfone which is supplied by Solvay Plastics were selected as the second polymer to be use in this study. Polyethersulfones contain sulfone and ether groups in the main chain. This polymer several excellent properties:

- ✓ High chemical resistance
- ✓ Stable to oxygen and to thermal degradation
- ✓ Good electrical insulation properties, which make it preferable to be use in electrical/electronic industries.
- ✓ Have high mechanical values
- ✓ Excellent resistance to combustibility

Polyethersulfones are unaffected by hydrocarbons and aqueous acids and bases, and only slightly affected by alcohols and detergent solutions. Figure 3.2 shows the chemical structure of Radel A Polyethersulfone. Chemical and Physical properties of this polymer were listed in Table 3.2.

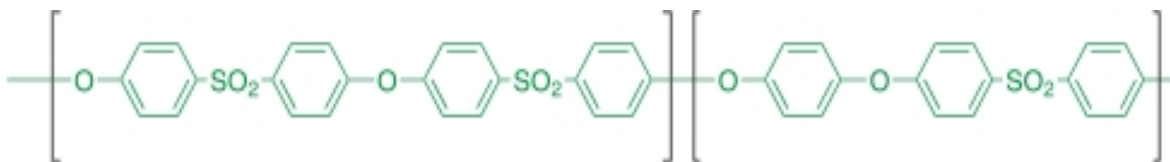


Figure 3.2: Chemical Structure of Radel A Polyethersulfone

Table 3.2: Chemical and physical properties of Matrimid[®] 5218 (Vu, 2001).

Properties	Value
Form	Pellet
Density (g/cm ³)	1.32
Glass transition temperature, T _g	220°C
Relative Thermal Index	180°C
Tensile Modulus	385 kpsia
Water Absorption, 24 hr at 23°C	0.54 %

3.2.2 Molecular sieve selection

The sieve used was synthetically produced commercially available zeolite 4A crystals from Aldrich. Zeolite 4A is the sodium form of Type A crystal structure, an alkali metal (Na₁₂[(AlO₂)₁₂(SiO₂)₁₂].xH₂O). Figure 3.2 shows the molecular structure of zeolite 4A.

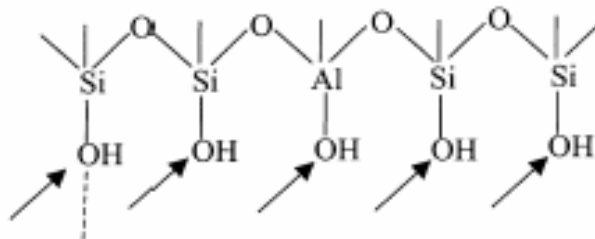


Figure 3.3: Molecular structure of zeolite 4A

The zeolite used were a white finely divided, free flowing powder with an average diameter of 5 microns with particles ranging from 3 to 19 micron (Qin, 1999). This particular zeolite was chosen due to its effective kinetic diameter of 3.8\AA makes it capable of discriminating between the oxygen and nitrogen molecules, the intended pair of interest. The sieves were dried in the vacuum over for 24 hours at 285°C before use to remove any water.

3.2.3 Solvent selection

NMP solvent is N-methyl-2-pyrrolidone, the lactam of 3-methylaminobutyric acid. It is synthesized by high pressure techniques based on Reppe Chemistry. Having no active hydrogen, this remarkably stable heterocyclic compound is classified as an aprotic solvent and is uniquely suitable as a chemical reaction medium.

NMP is chosen as the solvent because it has good chemical stability, high solvency and high boiling point. NMP solvent also eliminates the problems associated with many solvents presently in use. Its low flammability, low volatility, biodegradability, low aquatic toxicity and recyclability make it suitable as a replacement for hazardous solvents. It reduces VOC emissions and has no adverse effect on the ozone layer. Table 3.2 shows the chemical and physical properties of NMP.

Table 3.3: Physical and chemical properties of NMP

Properties	Value
<i>Molecular Weight</i>	99.1
<i>Purity (N-methyl-2-pyrrolidone)</i>	99.8% min
<i>Physical Form</i>	liquid with mild amine-like odor
<i>Moisture content</i>	0.05 % max
<i>Density (20 °c)</i>	1.03 gm/cc
<i>Boiling Point @ 760 mm</i>	202 °c
<i>Freezing Point</i>	-29.4 °c
<i>Specific Gravity</i>	1.027
<i>Flash Point</i>	93 °C

3.3 Penetrants

To carry out the gas permeation test, pure gas of O₂ and N₂ was purchased from Union Carbide. The pure gases were certified to have purity of 99.99% O₂ and 99.99% of N₂. Table 3.3 shows the properties for O₂ and N₂ gas.

Table 3.4: Properties of penetrant gases used in this study

Gas Molecule	Molecular Length Å	Molecular Width Å	Zeolite Seiving Diameter. Å	T _c (K)	P _c (atm)
O ₂	3.75	2.68	3.46	154.6	50.5
N ₂	4.07	3.09	3.64	126.2	33.7

3.4 Dope Solution Preparation

In mixed matrix membrane formation, the dope solution should contain three main materials which are (i) polymer, (ii) molecular sieve and (iii) solvent. The polymer may be commercially available or tailored materials with desirable intrinsic gas separation properties. The selected solvent must be able to fully dissolve the polymer used. If there is nonsolvent present in the solution system, the solvent must be the point of the incipient phase to tolerate with the nonsolvent so that the point of the incipient phase separation can be reached while maintaining the dope rheology that is appropriate for casting the membrane (Pinnau et. al, 1990). For mixed matrix membrane, the dope solution might be slurry in the presence of molecular sieve particles. The dope solution must be relatively concentrated since lower concentrations led to low viscosities and settling of the sieve phases in the film, which would produce a non-homogeneous morphology (Mahajan, 2000).

This experimental procedure has been conducted by a group of researchers from National University of Singapore with some modification been done. Initially, the purchased zeolites were dried in a vacuum condition at 80°C for at least 24 hours. This drying process is done to remove moisture content during storage. These molecular sieves then dispersed into NMP solution. Basically, about 10% wt of zeolite were dispersed into the solvent. The slurry solution was stirred for 4 hours to homogeneously distribute the zeolite particles in the solution. The slurry solution was then been sonicated in an ultrasonic bath for 1 hour. This is done to provide powerful shearing of the zeolite particles breaking up aggregates of particles and enhancing homogeneity during the intense agitation (Vu, 2001).

Figure 3.3 shows the apparatus for dope solution preparation. The round bottom solution vessel was used to prepare the solution. The function of stirrer is to make sure that the polymer and solvent can mix well in order to form a homogeneous solution. The thermometer measured the temperature during the mixing process. The processing temperature should be controlled in a suitable and optimum temperature range by the

heater and the condenser. In this study, the dope solution was prepared in a controlled temperature of 60°C to 80°C, which is the working temperature of NMP.

In order to remove all the water vapor from the polymer and equipment, they had been heated in the oven respectively at least for overnight before the solution was prepared. The existence of water in the polymer solution will influence the purity as well as quality of a polymer solution. Finally, the polymer matrix, which is consist of blend of Polyethersulfone and Matrimid[®] 5218 were added to the slurry, and the final slurry was stirred at a reduce velocity for another 12 hours. The quantity of zeolite particles and the amount of polymer added determined the “loading” in the final mixed matrix membrane. In this study, the “zeolite loading” is between 10% to 50% wt solids in the solvent. This could be considered a concentrate solution since viscous mixed matrix slurries could minimized the sedimentation and aggregation problems as stated before (Vu, 2001). The dope solution is now ready to go through membrane casting process.

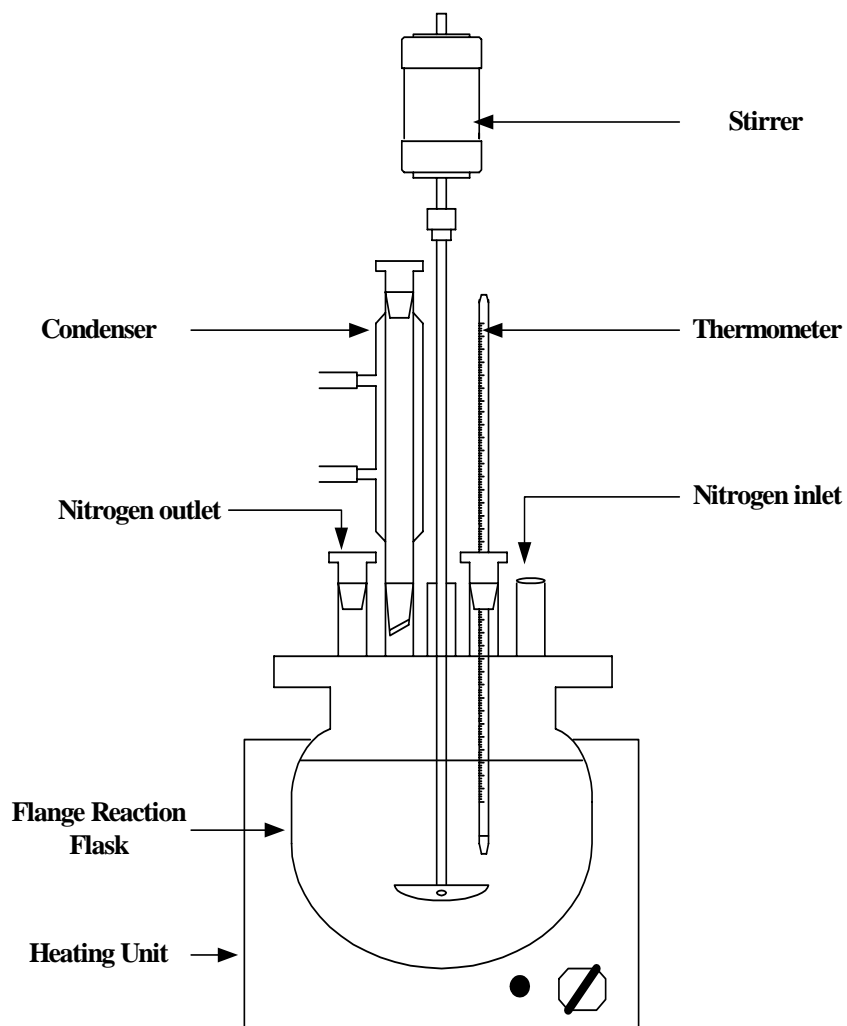


Figure 3.4 : Dope solution preparation vessel (Cheer, 2002)

3.5 Mixed Matrix Membrane Film Formation

The method for casting mixed matrix membrane solution is the same for homogenous and dense film. The polymer-sieve slurry is poured onto a clear, flat glass plate, as shown in Figure 3.4. The plate will be placed inside a plastic box. As before, a stainless steel film applicator (steel casting knife) is used to draw/spread the polymer-sieve slurry to a uniform thickness. The membrane film is then placed under a close environment, in order to slow down the evaporation rate of the solvent from the film

surface. The membrane film is placed under a plastic containing with some small opening to evaporate the solvent. The evaporation process is done for 12 hours.

To remove the membrane film from the glass plate, a razor blade is used to slightly peel the film from the glass surface to initiate delamination. Because water can physisorb or chemisorb to the carbon sieves, water was not used to delaminate the film as sometimes done for homogeneous, dense polymer films (Vu, 2001). The membrane film is then further dried after initial evaporation at temperature of about 100°C for at least 12 hours in a vacuum oven to remove residual solvent.

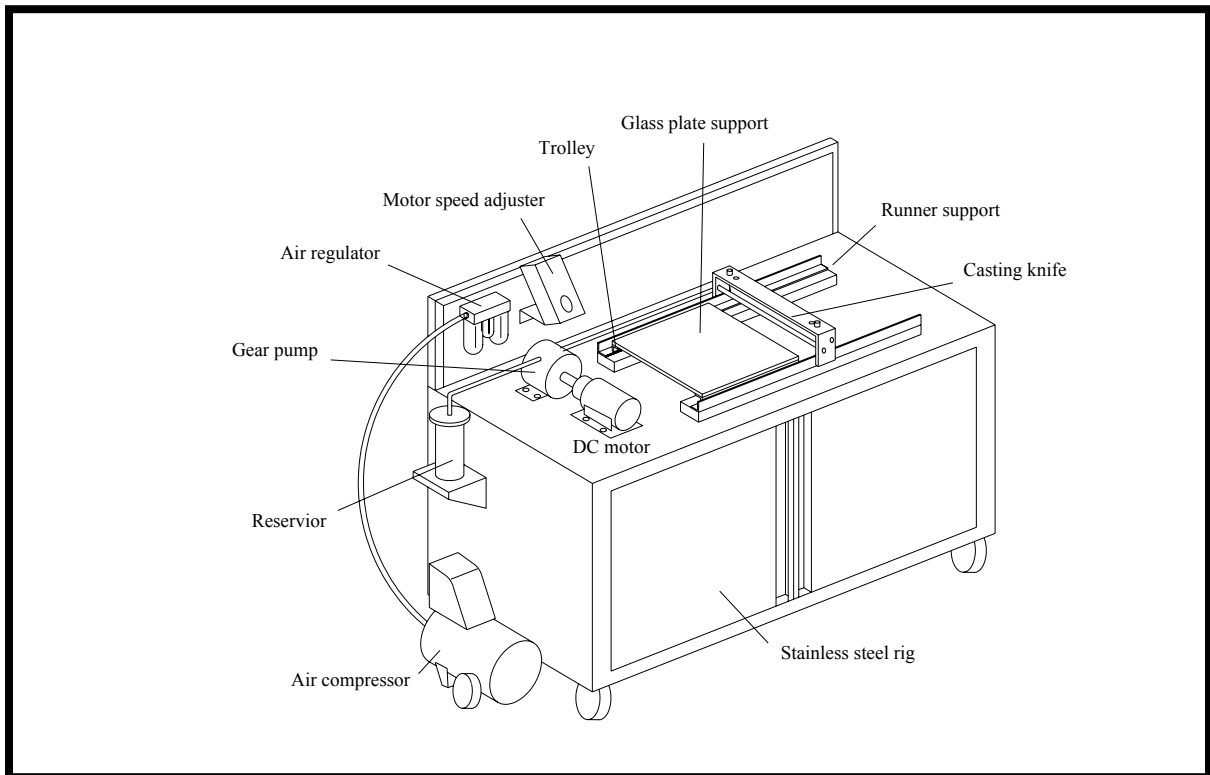


Figure 3.5: Schematic drawing of new designed semi-automation pneumatically-controlled flat sheet membrane casting machine (Cheer, 2002)

3.6 Treatment

3.6.1 Heat treatment

The dried mixed matrix films will be placed in a hot air oven (Shel Lab). Heat treatment for different temperatures will be carried out at temperature between 100 to 330°C for 15, 30 and 60 minutes, respectively. This treatment is done in order to suppress the plasticization of the membrane as well as to increase the effect of “sizing agent” to the membrane. The mixed matrix film is then cooled down naturally to 35°C. The cooled film is then taken from the oven and subsequently used for testing. The treated membranes are then characterized by pure gas permeation testing system.

3.7 Characterization

3.7.1 Differential Scanning Calorimetry (DSC)

This equipment is used to determine the glass transition temperatures of the film samples (Vu, 2001). Glass transition temperature, T_g is generally regarded as the temperature at which large-scale segmental motions becomes comparable to the time scale of the measurement. The glass transition temperature provides a qualitative measure of the flexibility or rigidity of polymer chains (Simha and Bayer, 1962). It is a useful tool for comparisons of the polymer chain rigidity of mixed matrix films at various CMS loadings to that of pure polymer films.

Raising T_g would reduce the rate of these motions at a certain fixed temperature. The glass transition temperature of the polymer is assumed to decrease as the heating temperature is further increased. This can be attributed as a more flexible polymer matrix or increase in chain mobility. This is mainly because the heat treatment near or above the glass transition temperature of the polymer may disrupt the chain rigidity.

3.7.2 Scanning Electron Microscopy (SEM)

The geometrical characteristics and the morphology of the developed mixed matrix membrane will be determined using scanning electron microscope (SEM). Images of fiber surface, skin layer structure and cross sections of membrane prepared under different carbonization condition can be viewed clearly. The dried films will be broken in liquid nitrogen and will be sputtered with a tin layer of gold using a sputtering apparatus. After that, the samples will be imaged and photographed by employing a scanning electron microscope (model Philips XL40).

3.7.3 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) will be performed in order to determine the weight loss of each sample as a function of temperature. At first, the sample will be measured in a crucible in the range of 10 to 12 milligram. The sample then will be mounted into a Mettler Toledo TGA Analyser, and will be heated from 30°C for 5 minute under nitrogen environment. The sample then further heated from 30°C to 1000°C with heating rate of 10°C/minute. The thermal behavior of a polymer can be characterized rapidly over a wide range of temperature in one experiment using a small amount of sample.

3.7.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a very useful tool to detect the existence of the functional groups in a membrane. The FTIR results can display changes of the functional groups and elements in the membranes when they are heated from room temperature to high temperature, which is up to 250°C. In this study, this characterization technique is important to show us the effect of polymer blending and zeolite adhesion to the molecular structure of the polymers.

3.7.5 Gas permeation test

Permeability measurements of the flat mixed matrix membrane films and pure polymer films are made using a constant volume where the upstream pressure is kept constant while measuring the flux across the membrane film (with known thickness and area of the permeate face) (Pye et al., 1976). The flux or permeation rate is measured from the pressure rise from the permeating gas in a known constant downstream (permeate) volume.

The new mixed matrix membrane is tested on pure gas O₂ and N₂. Pure gas permeation test is done to examine the separation ability of a fabricated membrane under ideal conditions. But in actual case, the transport of a component in a gas mixture through glassy polymeric membranes is affected by the presence of other penetrants either due to the composition among the permeating species or by plasticization of the polymers in the mixture contains certain hydrocarbons and CO₂. Therefore, mixed gas separation generally yields lower selectivities for membranes than those of pure gas measurements (Vu, 2001). The feed and retentate pressure are measured by pressure gauges.

3.7.6 Operation of Gas Permeation Testing Apparatus

Permeation tests of the membrane will be performed by introducing the upstream with the desired gas at the desired pressure. For pure gas permeation test, the upstream pressure is kept constant, while the downstream pressure is open to the atmosphere. Gas permeation test is done at room temperature. The pure gas will be tested at pressure in the range of 1 bar to 3 bar. The gases were specified as having a purity of 99.99%. Both gases are used without further purification. Figure 3.5 and Figure 3.6 shows the gas testing apparatus that will be used.

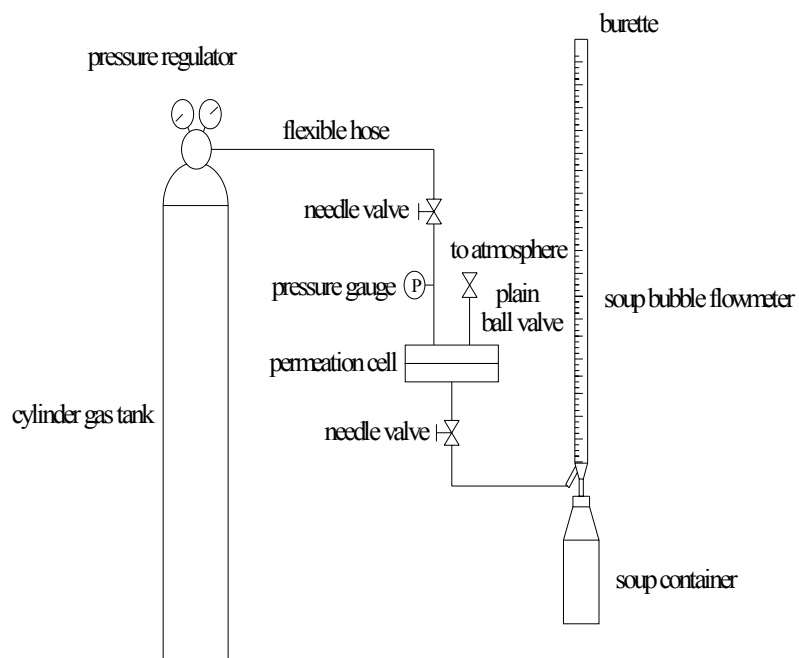


Figure 3.6: Gas permeation test apparatus (Cheer, 2002)

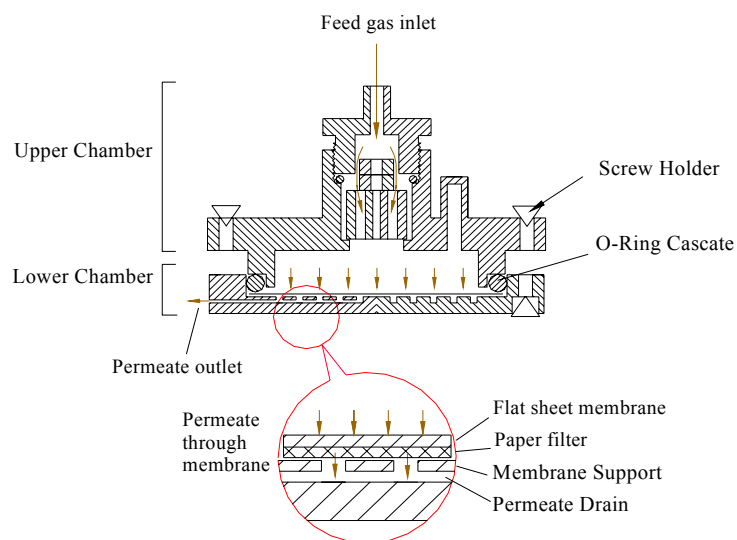


Figure 3.7: A cross-sectional view of assembled permeation cell and gas flow direction (Cheer, 2002)

CHAPTER IV

RESULTS AND DISCUSSION

This chapter will be discussing about the effect of polymer blending onto mixed matrix membrane performance. The changes in physical properties of the pure polymer will be determined using various characterization methods such as FTIR, DSC, TGA and SEM. It is expected that by incorporating polymer blending method in the mixed matrix membrane formation will help to improve the polymer-sieve contact since the blending involve two type of polymer with different physical and chemical properties. FTIR scan will show if there is any new bonding occur between Polyimide and Polyethersulfone molecule structure. If this happen, this showed that both polymer are compatible with each other. DSC scanning method will give us detail information on the thermal properties of this mixed matrix membrane. It is expected that by increasing zeolite loading will increase the glass transition temperature (T_g) of the membrane. The changes in thermal properties of the mixed matrix membrane will be detected by using TGA. Finally, SEM will give us a better view on the structure and how the was the condition of the polymer sieve contact of the mixed matrix membrane.

4.1 Polymer dope composition

The dope solution for mixed matrix membrane fabrication was prepared at basis of 100g solution. The zeolite loading were calculated based on wt %. Blends of Polyimide and Polyethersulfone were prepared using a 20 wt% solution in 1-Methyl-2-Pyrrolidinone (NMP) in three different proportions of PI/PES, which are:

- a) 80% PES/20% PI
- b) 50% PES/50% PI
- c) 80% PI/20% PES

Example of calculation:

For 100g dope solution with composition of 30% zeolite 4A in 80% PES, 20% PI, the calculation is:

$$\begin{aligned}\text{Solvent (NMP)} &= 80\% \text{ of dope solution} \\ &= 80/100 \times 100\text{g} \\ &= 80\text{g}\end{aligned}$$

$$\begin{aligned}\text{Volume in ml} &= 80\text{g} \times \text{density of NMP} \\ &= 80\text{g} \times 1000\text{ml}/1030\text{g} \\ &= 77.67\text{ml}\end{aligned}$$

$$\begin{aligned}\text{Polymer content} &= 20\% \text{ of dope solution} \\ &= 20/100 \times 100\text{g} \\ &= 20\text{g}\end{aligned}$$

$$\begin{aligned}\text{Composition of Polyethersulfone} &= 80\% \text{ of } 20\text{g} \\ &= 80/100 \times 20\text{g} \\ &= 16\text{g}\end{aligned}$$

Composition of Polyimide = 20% of 20g
= 20/100 x 20g
= 4g
zeolite loading = 30% of total weight (polymer + zeolite)
= 8.571g

Table 4.1 summarizes the dope solution composition for mixed matrix membrane fabrication in this study. There are 10 different composition prepared for this study.

Table 4.1 : Summary of dope solution composition for mixed matrix membrane

Dope solution (100g)	Composition (gram)			
	PES	PI	Zeolite (4A/3A/5A)	NMP
30% 4A in 80% PES / 20%PI	16	4	8.571	80
30% 4A in 50% PES/ PI	10	10	8.571	80
30% 4A in 80% PI / 80% PES	4	16	8.571	80
10% 4A in 50% PES/PI	10	10	2.222	80
20% 4A in 50% PES/ PI	10	10	5.000	80
40% 4A in 50% PES/ PI	10	10	13.333	80
50% 4A in 50% PES/PI	10	10	20.000	80
30% 3A in 80% PES/ 20% PI	16	4	8.571	80
30% 5A in 80% PES/ 20% PI	16	4	8.571	80
50% PI/ 50% PES	10	10	0	80

4.2 FTIR analysis

The most direct way to study the nature of polymer mixture is by using FTIR spectroscopy. FTIR spectra for pure polyethersulfone shows that the sulfonate groups

give the characteristic peaks at 1147.8cm^{-1} . Antisymmetric C-O stretching frequencies occur at 1237.7cm^{-1} and 1011.7cm^{-1} , while absorptions in the range of 1578.2cm^{-1} to 1485.4cm^{-1} region are associated with the benzene ring stretching mode. While for pure Matrimid 5218, the carbonyl groups of Polyimide give a characteristic peak at 1719.9cm^{-1} . The C-N primary and secondary vibrations are shown in the range of 1248.5cm^{-1} to 1367.7cm^{-1} .

For a membrane consists of miscible blends, frequency shifts usually indicate specific interactions between the characteristic group of the pure polymers. Figure 4.2.1 shows the FTIR spectra for pure polymeric membrane with Matrimid 5218/ Polyethersulfone blends at composition 50-50. This FTIR spectra shows the observed frequency shifts and absorption intensity changes for the characteristic groups of pure polymer., while figure 4.2.2 shows the FTIR spectra pure 4A zeolite.

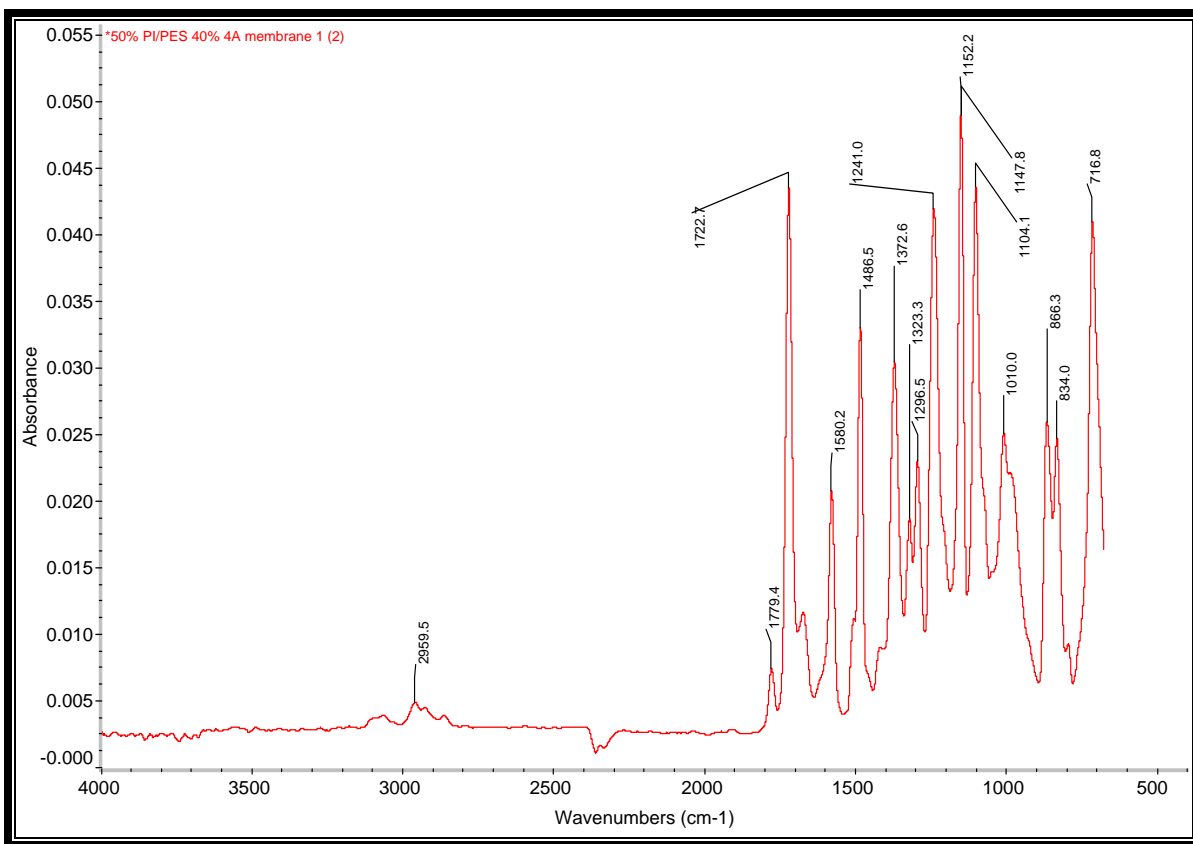


Figure 4.2.1 FTIR spectra for pure polymeric membrane consists of PI/PES blends at composition of 50-50

Figure 4.2.1 shows some frequency shifts and intensity changes, for the characteristic groups of the pure polymers. The frequency shift is observed for the polyimide carbonyl group (from 1719cm^{-1} to 1723cm^{-1}), while secondary shifts are observed for the aromatic carbon-oxygen stretching vibration frequency, which is from 1248cm^{-1} to 1241cm^{-1} . The benzene ring stretching mode shift from 1587cm^{-1} to 1580cm^{-1} and the aliphatic hydrogen vibration shift from 1370cm^{-1} to 1372cm^{-1} .

Changes in absorption intensity are observed for the sulfonate groups, which is stretching vibration at 152cm^{-1} and the aromatic carbon groups, with vibration frequency at 1486cm^{-1} . These spectra shifts and intensity changes suggest Polyimide and Polyethersulfone interactions and mixing at molecular level. Therefore, these structure analysis results support further the compatible nature of PI/PES blend membranes indicated by the microscopic and macroscopic observations.

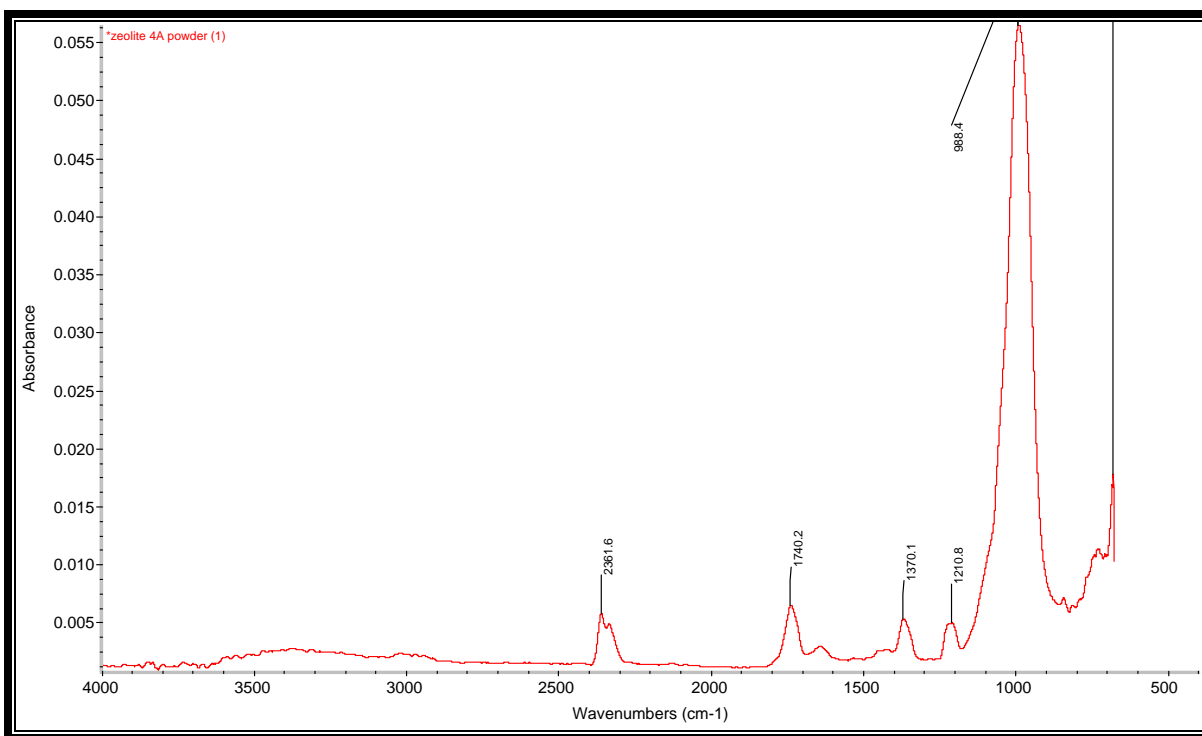


Figure 4.2.2 FTIR spectra for zeolite 4A powder

Figure 4.2.3 shows the FTIR spectra for mixed matrix membrane with 50% 4A zeolite loading at blend composition of 50-50. the strongest absorption is observe for frequency shift from 988cm^{-1} to 987cm^{-1} , which give the characteristic of the absence of zeolite in the membrane. Figure 4.2.4 and figure 4.2.5 shows the FTIR spectra for mixed matrix membrane with zeolite 3A and 5A, respectively. The major difference is for the absorption peak at 1000cm^{-1} , which characterize the zeolite 3A and 5A.

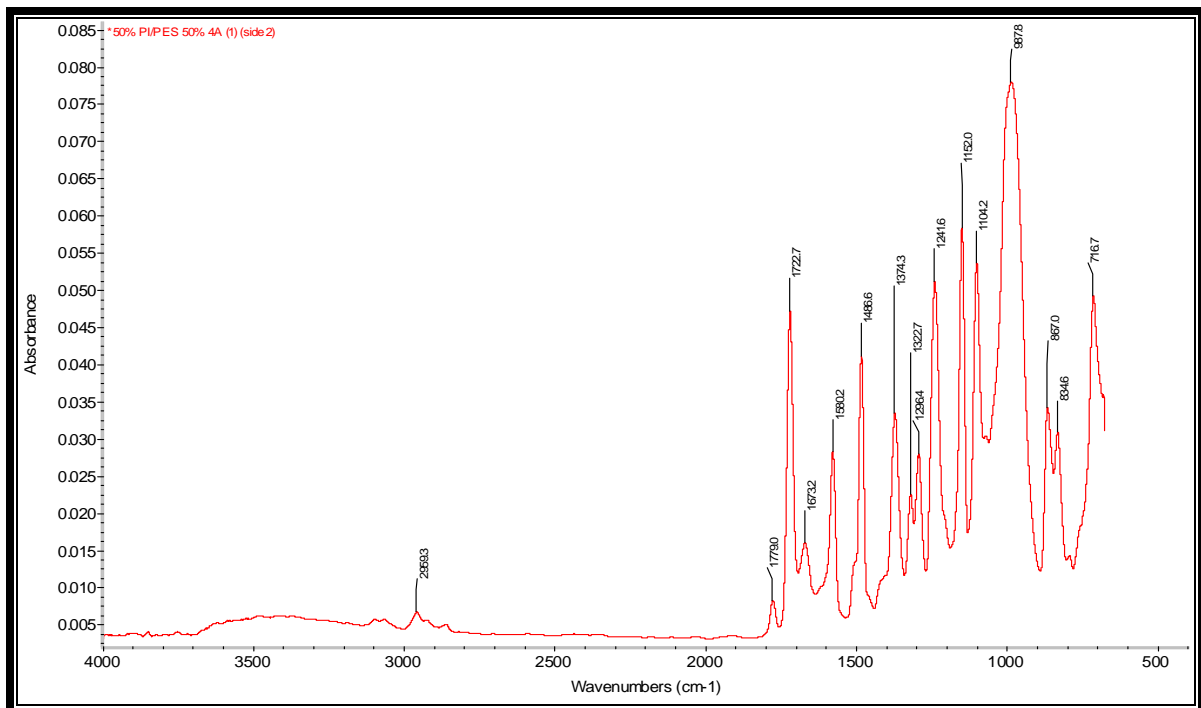


Figure 4.2.3 FTIR spectra for mixed matrix membrane with 50% 4A zeolite loading in PI/PES blends at composition of 50-50

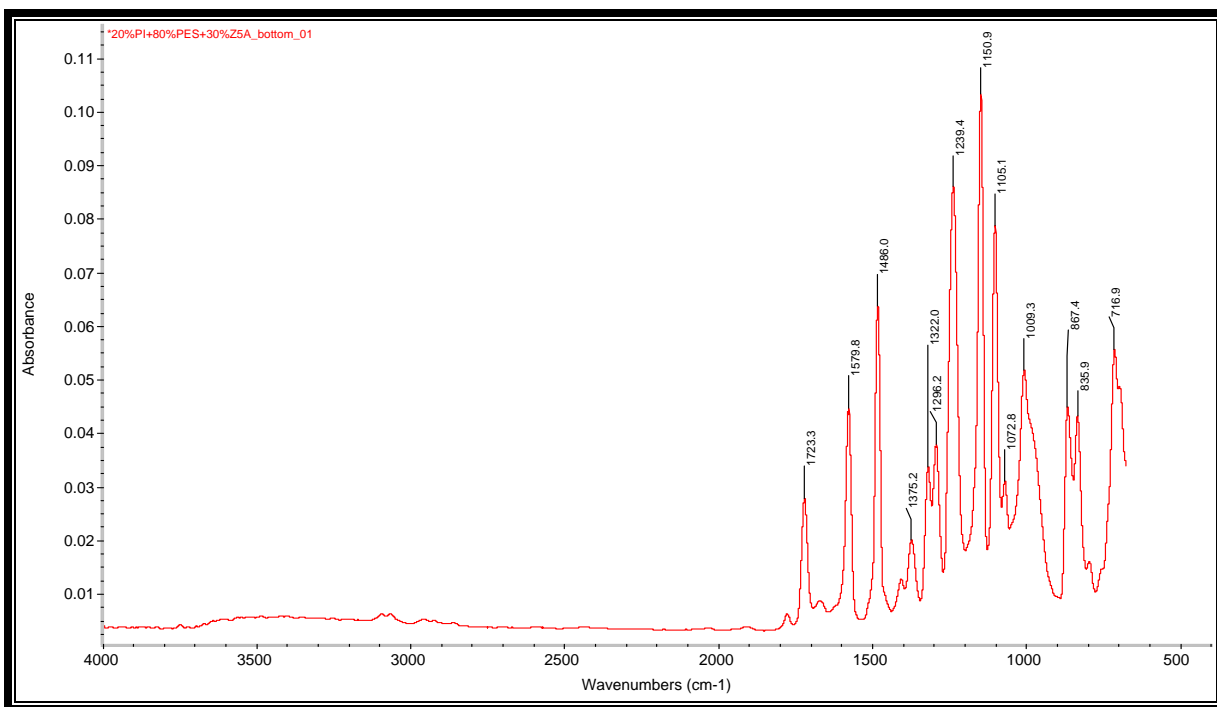


Figure 4.2.4 FTIR spectra for mixed matrix membrane consists of 30% 5A zeolite loading in PI/PES blends at composition 20-80

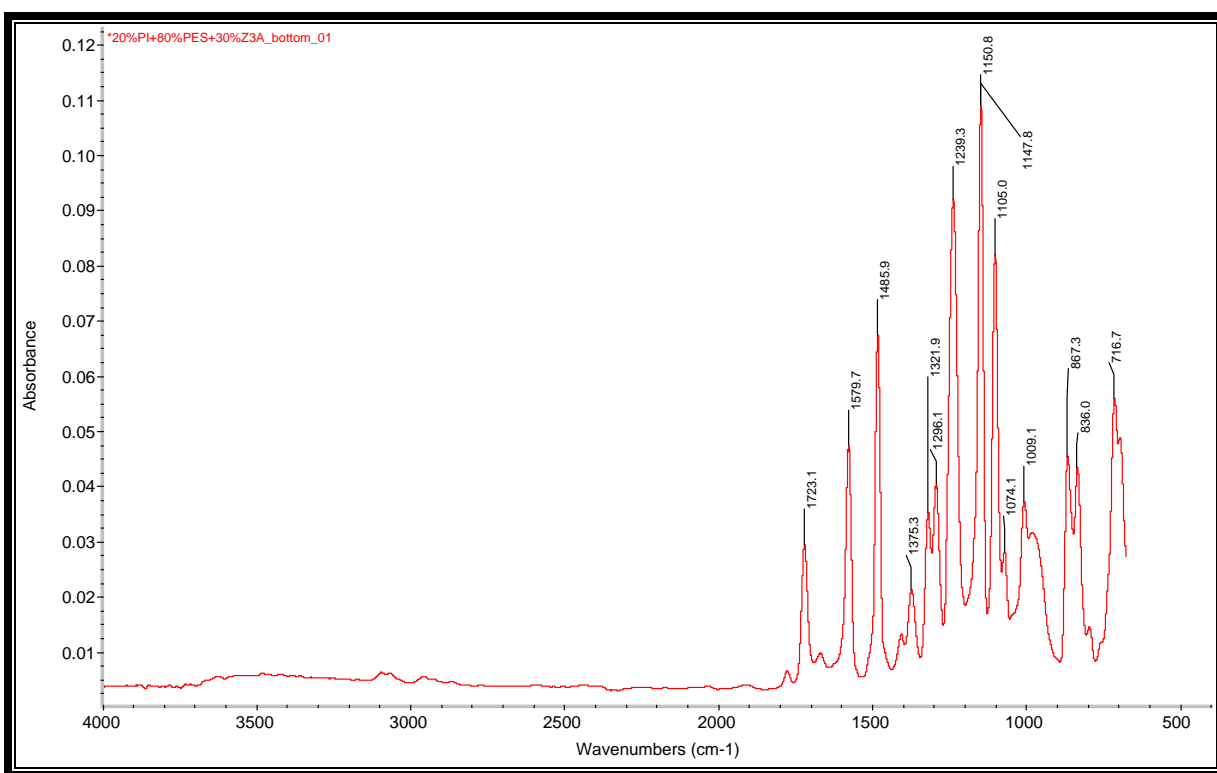


Figure 4.2.5 FTIR spectra for mixed matrix membrane consists of 30% 3A zeolite loading in PI/PES blends at composition 20-80

4.3 Effect of Polymer Blending on to the Polymer Glass Transition Temperature of Mixed Matrix Membrane

Macromolecules can be tailored to control interchain displacements and segmental mobilities. Likewise, the chains of a given polymer can be packed to various extents to control density and pressure-normalized flux. Such control can be effected by thermal means. At 50°C below the T_g , segmental mobility is very restricted, so the interchain displacements are fixed. Diffusive selectivity is based on the inherent ability of polymer matrices to function as size and shape-selective media. This ability is primarily determined by such factors as polymer segmental mobility and intersegmental packing. This kinetic sieve model sufficed to account for the principal features of many of the important gas separations, including those involving H_2/N_2 , H_2/H_2 hydrocarbons and O_2/N_2 (Kesting and Fritzsche, 1993).

In this study, the T_g of the fabricated mixed matrix membrane is determined using DSC. Measurements were performed on a Mettler Toledo DSC at a heating rate of 10°C/min. Membrane samples of 4-8 mg were cut from the membrane for DSC measurement. The T_g for both pure polymers used for this study had been determined earlier. For pure Matrimid 5218 which had been purchased from Alfa Aesar, the T_g is 324.57°C, while for Radel A Polyethersulfone from Solvay is 222.05°C. DSC scans of the membrane consist of Matrimid 5218/Polyethersulfone of different composition and zeolite loading, indicating one single glass transition temperature. Figure 4.3.1 shows the DSC result for pure polymeric membrane without zeolite. The T_g for the membrane which consists of blends of Matrimid 5218/Polyethersulfone blends at the blend composition 1:1 is 223.59°C. The indication of one T_g of the membrane confirms that both polymers are miscible with each other. The Matrimid slightly helps to stabilize the interchain of pure polyethersulfone structure by slightly increasing the T_g of pure Polyethersulfone.

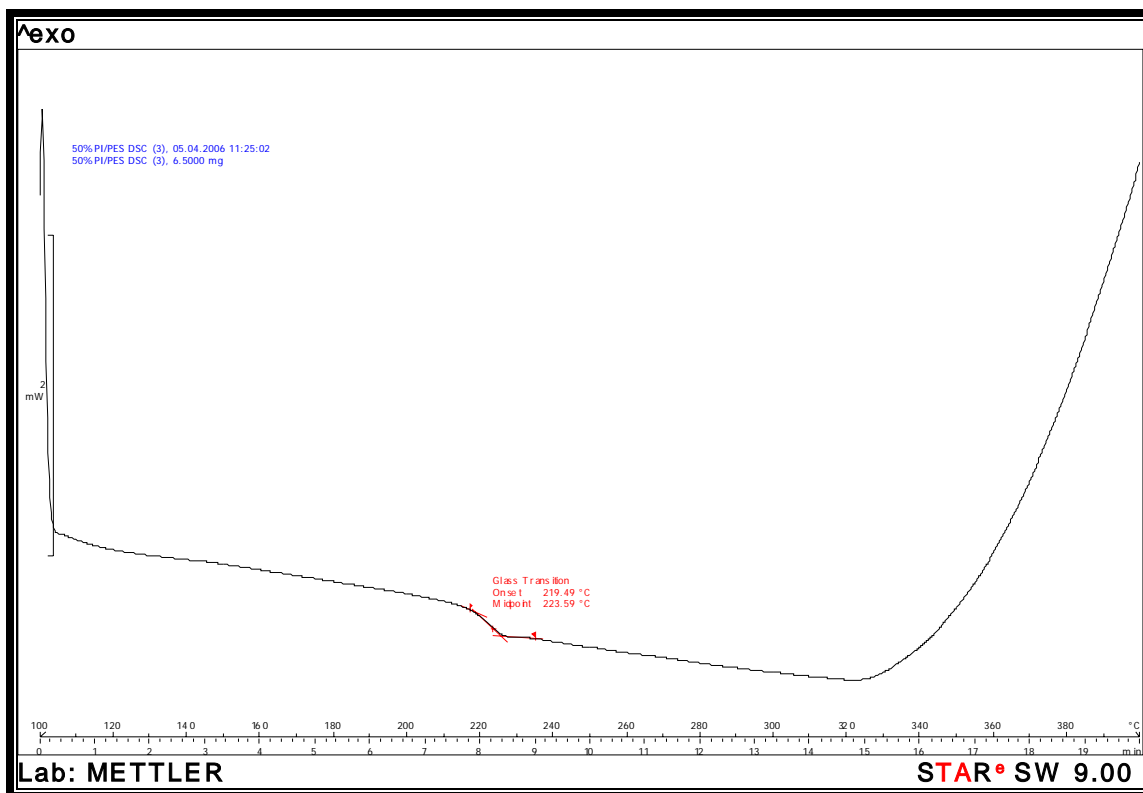


Figure 4.3.1: DSC scan of PI/PES blends membrane with composition of 50-50.

It is understood that by increasing the zeolite loading onto the mixed matrix membrane will increase the T_g of the pure polymeric membrane. Figure 4.3.2 shows the effect of zeolite loading on the T_g of mixed matrix membrane. The blends composition of the membrane is constant. By adding more zeolite, the free volume of the polymer chain will be lesser since it has been occupied by the molecular sieve. The zeolite will restrict the movement of the molecular chain, which causes the glass transition temperature to increase.

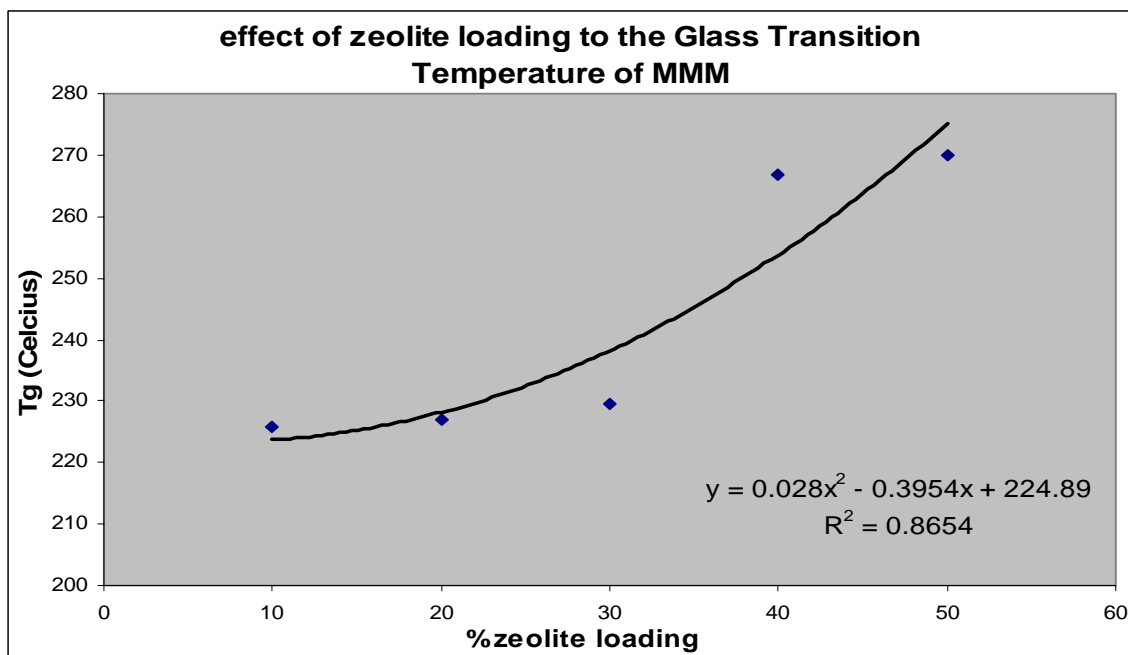


Figure 4.3.2 : Effect of zeolite 4A loading on to the glass transition temperature of mixed matrix membrane

In this study, we also study three different type of zeolite. Figure 4.3.3 shows the effect of type of zeolite onto the glass transition temperature of the mixed matrix membrane. From the figure, the mixed matrix membrane which content zeolite 4A give the highest glass transition temperature, followed by membrane with zeolite 3A and 5A. this may due to the bigger size of zeolite 4A, which is in the size of 5 μ m. Even though the 4A zeolite is a commercial obtain, it has to be sieve before adding into the dope solution, compared to zeolite 3A and 5A which has a very fine small particle size. With bigger size of zeolite, more free volume of the polymer chain could be occupy. This will hinder the movement of the polymer chain, thus increase the glass transition temperature of the mixed matrix membrane.

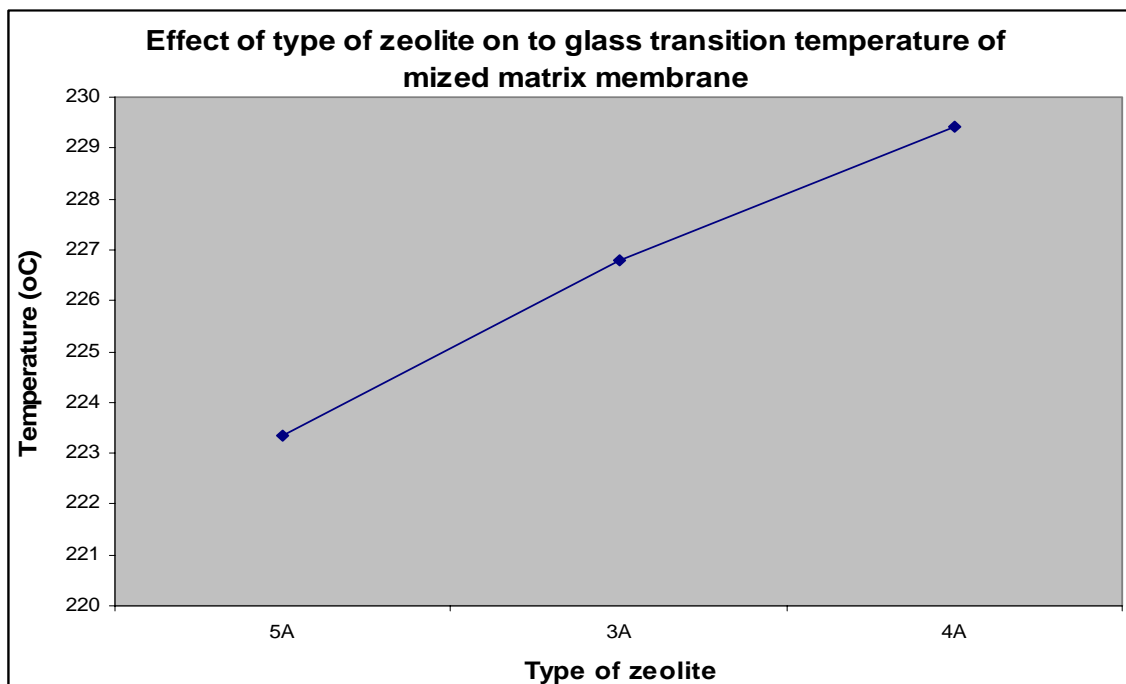


Figure 4.3.3 : Effect of type of zeolite on to the glass transition temperature of mixed matrix membrane

Figure 4.3.3 shows the effect of PI/PES blends composition onto the glass transition temperature of the mixed matrix membrane. The highest T_g achieve is for the mixed matrix membrane with PI/PES blends composition of 80-20, which is 328.97°C. The T_g of this membrane is very closed to the T_g of pure Polyimide membrane. This could be explain by the percentage of the pure polymer in the membrane. Polyimides are rigid, has high T_g , thermally stable polymers formed by the condensation reaction of dianhydrides with diamines (Allcock and Lampe, 1990). With higher Polyimide content, this polymer seems to control the thermal properties of the membrane.

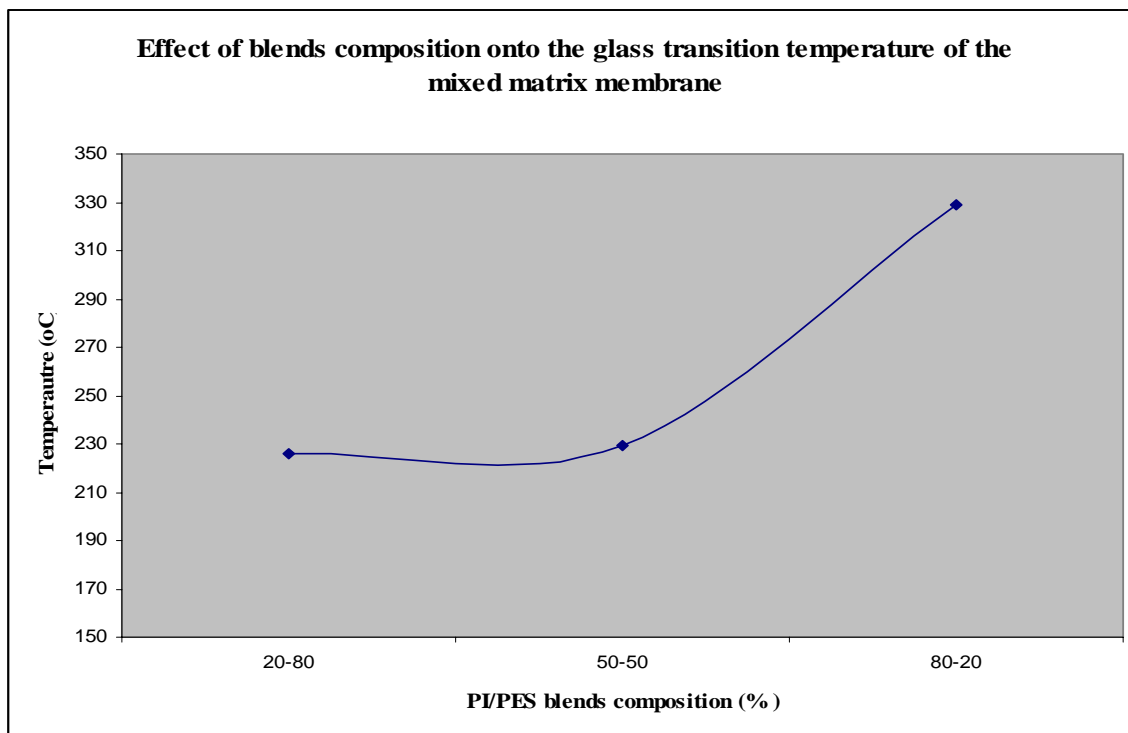


Figure 4.3.4 : Effect of blends composition on to the glass transition temperature of mixed matrix membrane

4.4 SEM analysis

The compability of two indicate polymer materials to form miscible blend mixtures can also be evidenced by optical measurement. SEM measurement can reveal the possible existence of phase separation in the polymer mixture. In immiscible blends, clear phase distinction is observed as the result of incompatibility of the pure polymers. Blending of Matrimid 5218 and Polyethersulfone results in complete mixing, with no phase separation, as shown in figure 4.4.1, for a clear, homogenous membrane of 50-50 PI/PES.

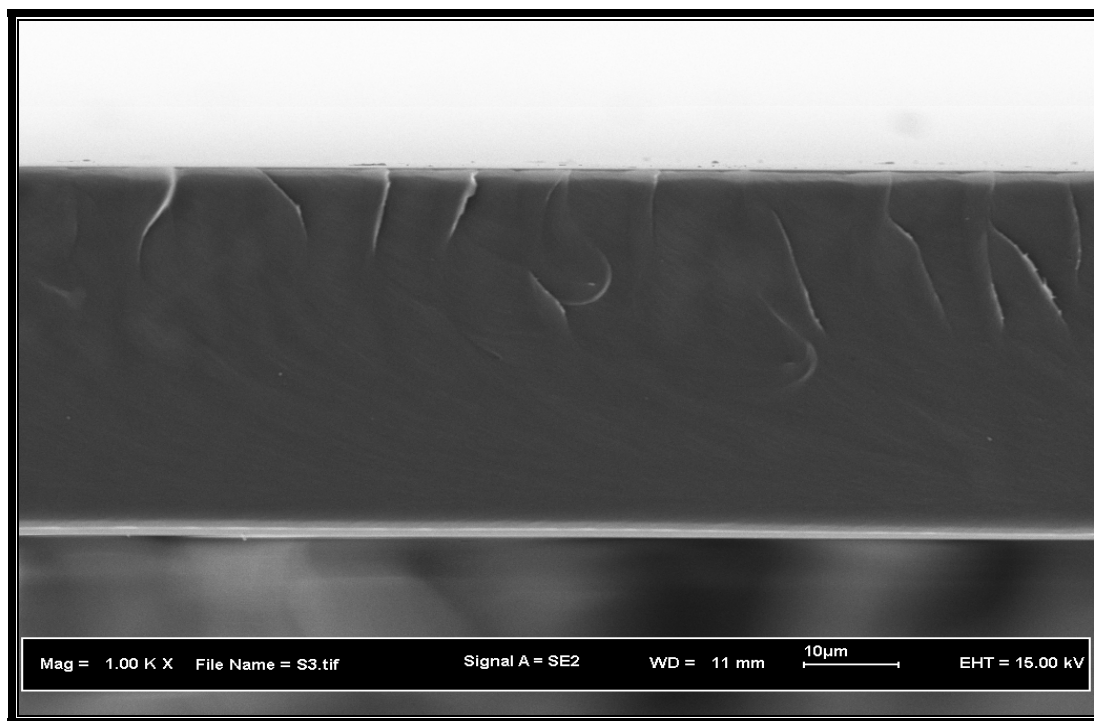


Figure 4.4.1 SEM picture of a PI/PES blends membrane with 50-50 composition at x1000 magnification

Figure 4.4.2 and figure 4.4.3 showed the SEM picture of mixed matrix membrane with 10% and 50% zeolite loading respectively, while the PI/PES composition is 50-50. Even though both polymer are good compatible with each other, but the blend matrix shows poor contact to the zeolite surface. It is understand that with increasing zeolite loading, the mixed matrix membrane tends to create more free volume surrounding the zeolite surface. These free volume are so called voids, which hinder the gas to pass through the zeolite. The presence of polar groups from Matrimid backbone only exhibit interchain packing in these Polyethersulfone, with the increasing of glass transition temperature of the membrane, but have poor interaction with zeolite surface. These voids will give an alternative path for the gas to pass through without observing the effect of molecular sieving. Thus, the resultant gas permeation will be higher but the selectivities decreased with increasing zeolite loading.

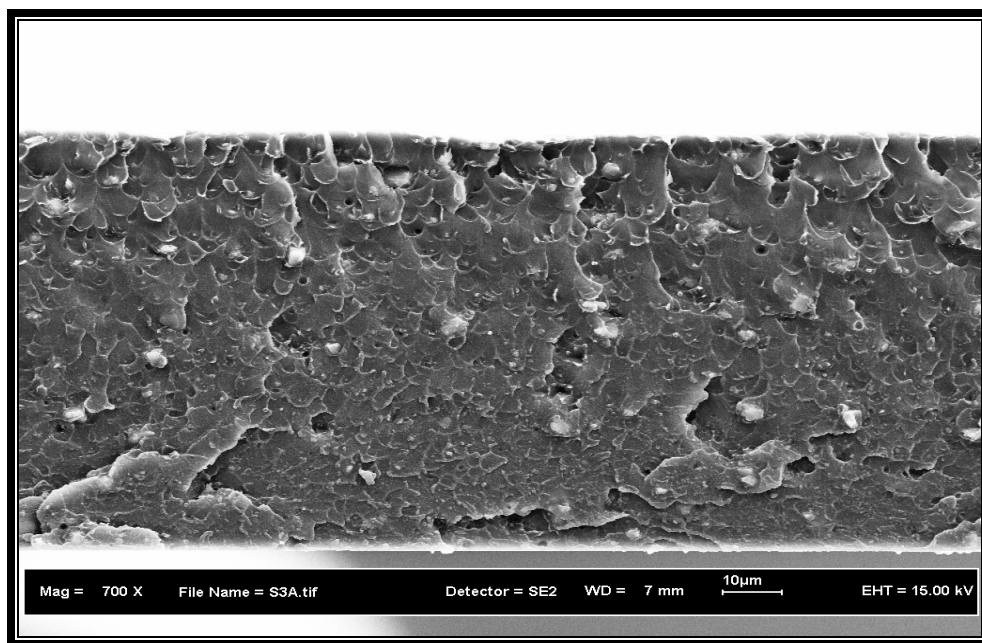


Figure 4.4.2 SEM picture for a PI/PES blends membrane at 50-50 composition with 10%4A zeolite loading

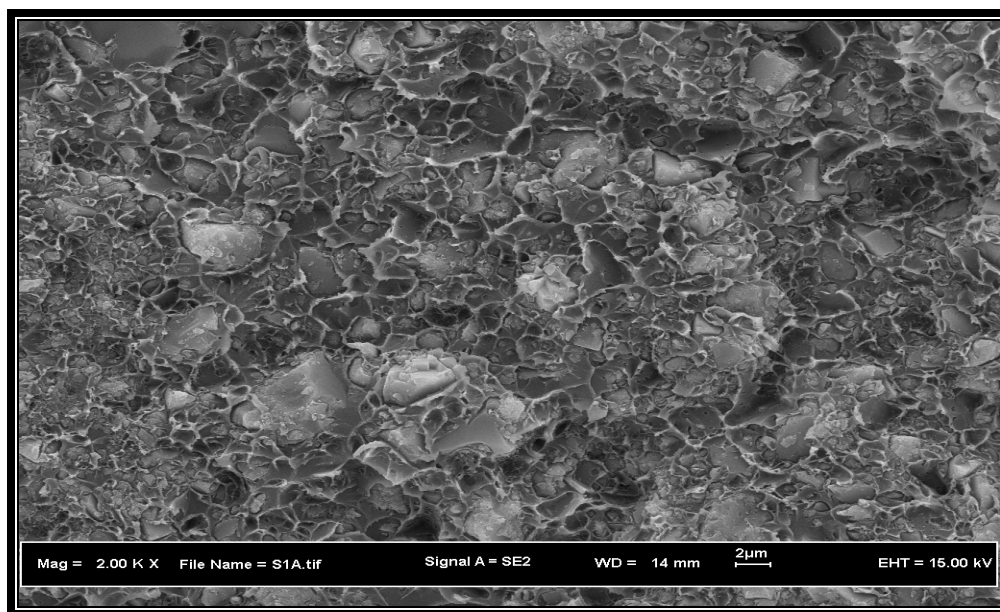


Figure 4.4.3 SEM picture for a PI/PES blends membrane at 50-50 composition with 10%4A zeolite loading. Poor polymer-sieve contact is observed.

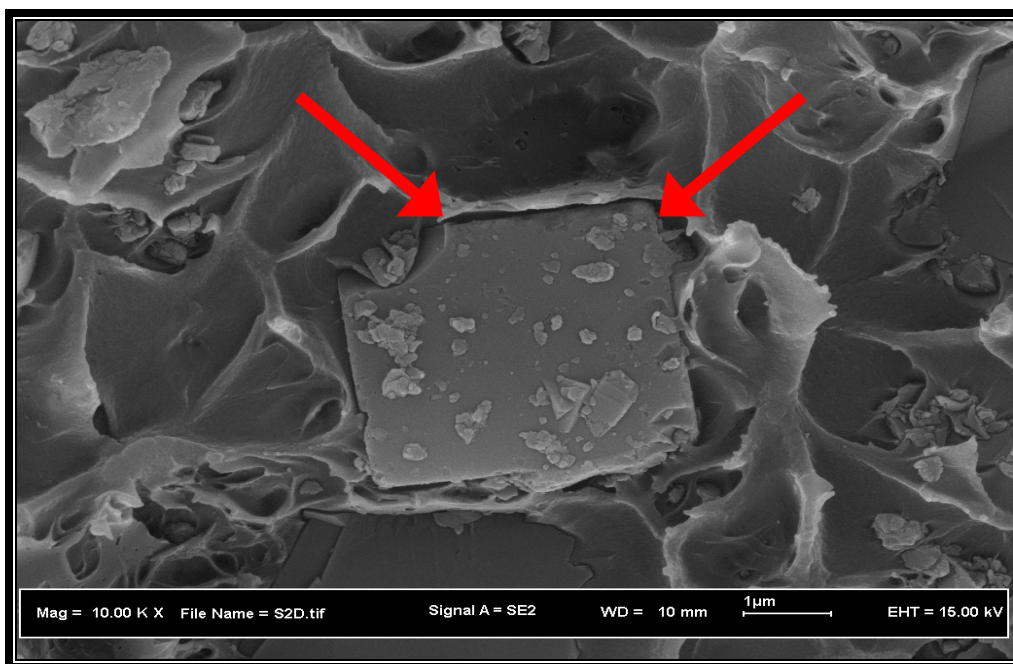


Figure 4.4.4: SEM picture for a PI/PES blends membrane at 20-80 composition with 30% 4A zeolite loading. Arrows showing the voids form between polymer matrix and zeolite surface.

4.5 TGA analysis

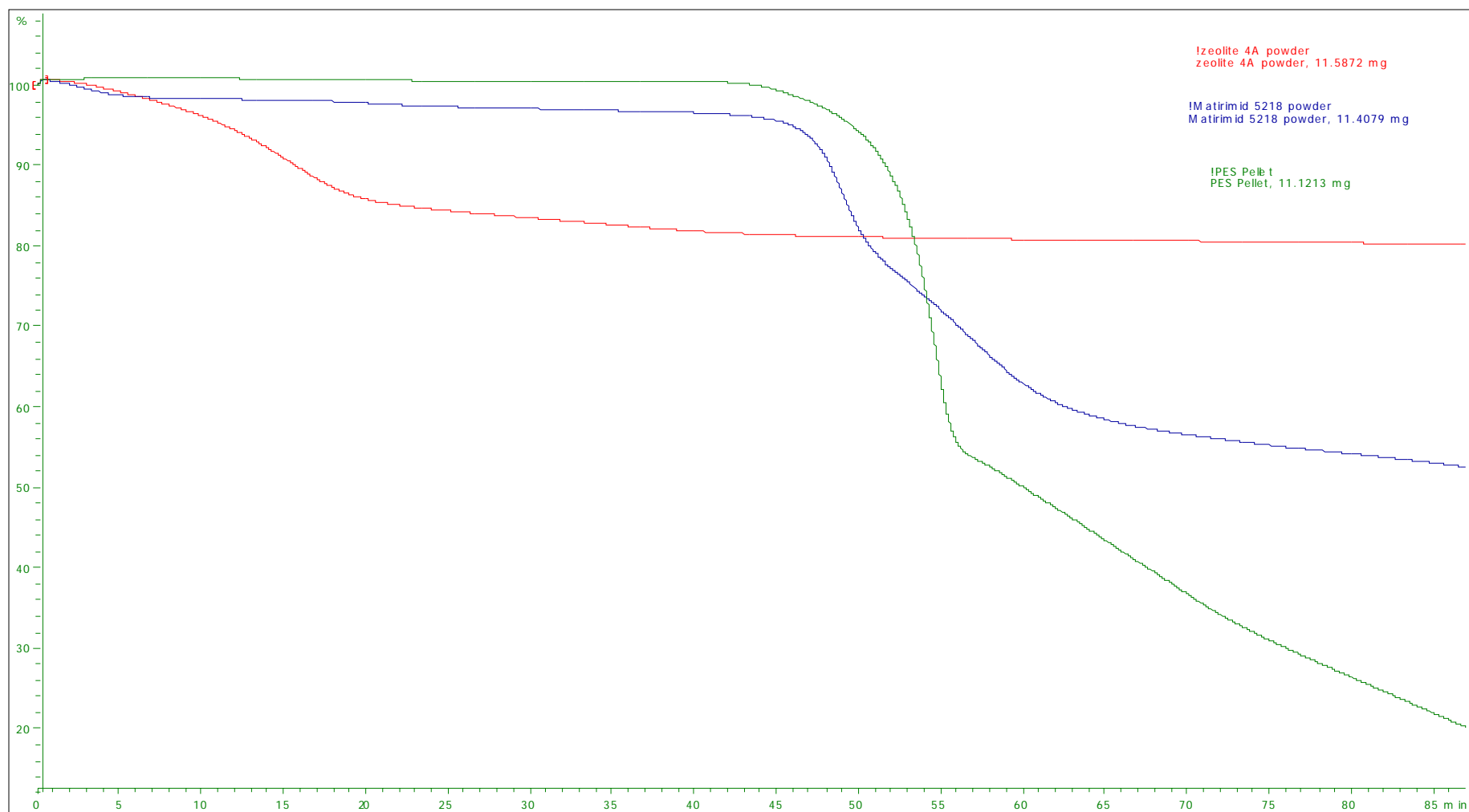
Thermogravimetric Analysis (TGA) will be performed in order to determine the weight loss of each sample as a function of temperature. This analysis was performed on the mixed matrix membrane samples with different zeolite 4A loading. By performing this measurement, we can also determine the effect of zeolite loading onto the thermal stability of the membrane. Under nitrogen environment, the samples were heated from 30°C to 1000°C at 100°C/min.

Figure 4.5.1 shows the weight changes as a function of temperature for pure polymers and zeolite 4A. At the temperature below 490°C, Matrimid 5218 shows a greater decrease in weight percentage with increasing temperature compared to Polyethersulfone. Seems Matrimid 5218 have limited molecule orientation with higher

T_g, this situation may be due to moisture content that is trapped in the membrane film. This could be eliminated by drying the membrane film at longer time with higher drying temperature. At higher temperature, Matrimid 5218 demonstrates better thermal stability compared to Polyethersulfone. In the case of zeolite 4A, the loss in weight only due to some moisture content, seems zeolite only composed of metal.

The weight changes for mixed matrix membrane as a function of temperature were shown in figure 4.5.2. When defining the degradation temperature as the temperature where 20% weight loss is achieved, the polymers exhibit degradation temperature of 500°C-540°C. At temperature below 500°C, the thermal stability for mixed matrix membrane decreases with increasing zeolite 4A loading. Membrane with 10% 4A zeolite loading is likely the most stable in this range of temperature. This result may arise from the increasing formation of voids and free volume between the polymer matrix and zeolite surface. These voids could store larger volume of moisture. Therefore, the loss in weight percent is contributed by the loss of moisture content.

From figure 4.5.2, we could see that two stages of degradation occur for mixed matrix membrane with higher zeolite loading. At temperature between 480°C to 520°C, mixed matrix membrane with 50% zeolite loading experiences rapid loss in weight percentage, which is a drop by 10%wt. But at a higher temperature between 520°C to 570°C, the thermal stability of the membrane seems to increase. This situation may be due to some interactions that occur between zeolite 4A and the polymer matrix, which helps to stabilize the polymer chain of the mixed matrix membrane. From here, we could see that the effect of zeolite loading did have some control over the thermal degradation of the mixed matrix membrane. Considering the measured degradation temperature, we could summarize that these materials exhibit considerable thermal stability, which most likely results from the membrane structure.



Lab: METTLER

STAR[®] SW 9.00

Figure 4.5.1 TGA analysis of pure Polyimide, pure Polyethersulfone and zeolite 4A

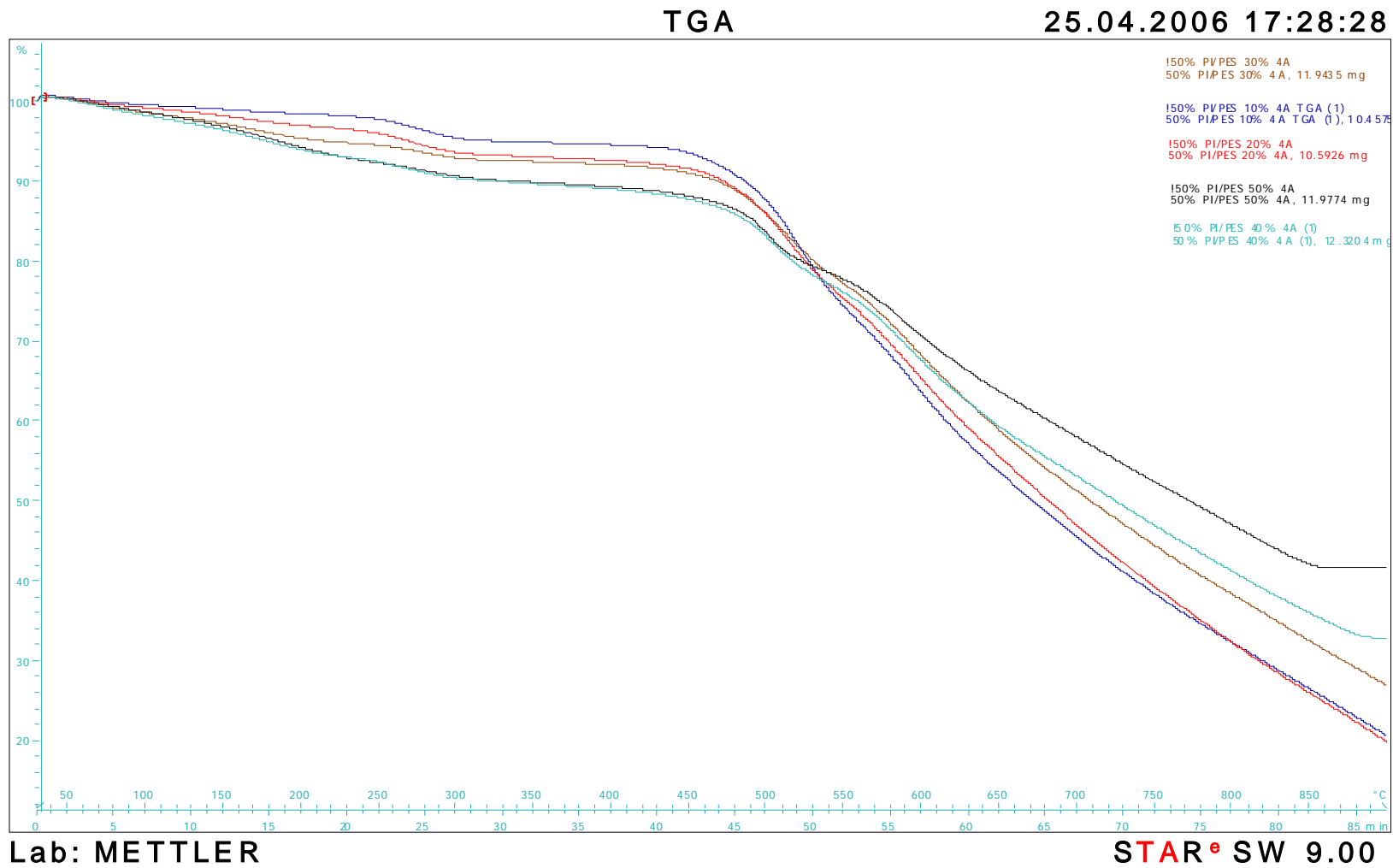


Figure 4.5.2 TGA analysis showing the effect of zeolite loading on the thermal stability of the mixed matrix membrane with PI/PES blends composition of 50-50

CHAPTER V

CONCLUSION AND FUTURE WORKS

5.1 Summary

In this study, the performance of mixed matrix membrane were studied by investigating four major aspects, which are i) the effect of polymer blending on to mixed matrix membrane performance, ii) the effect of zeolite loading, iii) the effect of dope composition and iv) the effect of type of zeolite onto the mixed matrix membrane performance.

Three main material been used in this study are Matrimid 5218 and Polyethersulfone as the blends matrix, while zeolite as the sieve matrix. The effect of type of zeolite had been investigate using zeolite 4A, 3A and 5A. The Matrimid 5218/Polyethersulfone blends composition had been varied to three different composition which are 80-20, 50-50 and 20-80. The fabricated membrane had been tested for gas separation by using highly pure gas O² and N². Finally, in order to check the physical and chemical properties of the fabricated mixed matrix membrane, numerous characterization method had been done using FTIR, DSC, TGA and SEM.

5.2 Conclusion

The conclusions can be made from this study are:

1. Blends of Matrimid 5218 and Polyethersulfone do exhibit a well homogenous mixture. This could be approve by the FTIR analysis which shows some peaks shifted due to interaction between both polymers. Thermal analysis which is measure by DSC scanning also prove that only one glass transition temperature occur for all mixed matrix membrane with different zeolite loading at different blends composition.
2. From all the characterization done onto the mixed matrix membrane, we could clearly see the effect of zeolite loading. with increasing zeolite loading, the resultant membrane obtain higher glass transition temperature compared to pure polymeric membrane. This is because the molecular sieve had occupied the free volume of the polymeric chain, causes the limited orientation of the molecular chain.
3. Effect of zeolite loading does contribute to stabilization of the thermal properties of the membrane. From the TGA measurement, it is clearly shown two stage of degradation occurred for mixed matrix membrane with higher zeolite loading, especially for the membrane with 30% to 50% zeolite loading. This may due to some interaction occurred between zeolite surface and polymer matrix.
4. Studies has been done on three different zeolite loading, which is zeolite 4A, 3A and 5A. The zeolite particulate size does effect the glass transition temperature of the mixed matrix membrane. Mixed matrix membrane with zeolite 4A shows the highest T_g compared to others, seem it has bigger size and higher molecular weight.

5. By adding the effect of polymer blending into mixed matrix membrane fabrication, it is expected to improve the gas separation performance of the membrane since both polymers have their own special physical and chemical properties. Anyhow, the SEM picture clearly show that voids formation occur between the polymer matrix and zeolite surface. This poor polymer-sieve contact give additional path for the gas to pass through without have to pass through the molecular sieve. This caused the gas permeation to increase while the selectivity decreases.

5.3 Recommendation for future work

Based on the results and conclusions obtained, the following recommendations arise in order to further improve the polymer-sieve contact thus improving the gas separation performance of the mixed matrix membrane.

1. The main problem in this study is the poor polymer-sieve contact. This could be eliminated by doing treatment, whether during the membrane preparation or during drying process. Some compatibilizer such as 2,4,6-triaminopyrimidine (TAP) could be added to eliminate the interfacial voids. In fact, filling the space between zeolite particles and polymer chains would be more convenient and effective than surface treatment of zeolite (Yong,2000). When the voids is minimize, the molecular sieving effect of zeolite could be clearly observed.
2. In order to have a better result of TGA analysis, the membrane should be further dried at longer time. This could help to remove the moisture content that is stored in the interfacial voids, thus the thermal degradation properties of the membrane could be more clearly observed

3. Further study on the effect of blending onto the mixed matrix membrane performance could be done using other pairs of miscible polymers, such as blend of Polysulfone and Polyimide. This may contribute to a better knowledge in the field of mixed matrix membrane.

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