GAS PERMEATION PROPERTIES OF POLY(ARYLENE ETHER KETONE) AND ITS MIXED MATRIX MEMBANES WITH POLYPYRROLE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

GÖRKEM MERGEN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

THE DEPARTMENT OF POLYMER SCIENCE AND TECHNOLOGY

JULY 2003

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Ali Usanmaz
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis and for the degree of Master of Science.

Prof. Dr. Levent Toppare
Supervisor

Prof. Dr. Levent Yılmaz
Co-Supervisor

Examining Committee Members

Prof. Dr. Ali Usanmaz (Chairman)

Prof. Dr. Levent Yılmaz

Prof. Dr. Levent Toppare

Prof. Dr. Ahmet Önal

Assist. Prof. Dr. Göknur Bayram

ABSTRACT

GAS PERMEATION PROPERTIES OF POLY(ARYLENE ETHER KETONE) AND ITS MIXED MATRIX MEMBRANES WITH POLYPYRROLE

Mergen, Görkem

M.S., Department of Polymer Science and Technology

Supervisor: Prof. Dr. Levent Toppare

Co-Supervisor: Prof. Dr. Levent Yılmaz

July 2003, 79 Pages

For the last two decades, the possibility of using synthetic membranes for industrial gas separations has attracted considerable interest since membrane separation technologies have the advantages of energy efficiency, simplicity and low cost. However, for wider commercial utilization there is still a need to develop membranes with higher permeant fluxes and higher transport selectivities.

Conductive polymers, due to their high gas transport selectivities, give rise to a new class of polymeric materials for membrane based gas separation though poor mechanical properties obstruct the applications for this purpose of use. This problem led researches to a new idea of combining the conducting polymers with insulating polymers forming mixed matrix composite membranes.

In the previous studies in our group, polypyrrole was chosen as the conductive polymer, and different preparation techniques were tried and optimized for membrane application. As the insulating polymer, previously poly(bisphenol-A-carbonate) was used to support the conductive polymer filler in order to constitute a conductive composite membrane. For this study, as the polymer matrix, hexafluorobisphenol A based poly(arylene ether ketone) was targeted due to its physical properties and temperature resistance which can be important for industrial applications.

First of all, permeabilities of N_2, CH_4, Ar, H_2, CO_2, and H_2 were measured at varying temperatures ranging from 25°C to 85°C through a homogenous dense membrane of chosen polymeric material to characterize its intrinsic properties. Measurements were done using laboratory scale gas separation apparatus which makes use of a constant volume variable pressure technique. The permeability results were used for the calculations of permeation activation energies for each gas. These permeation activation energies were found to be differing slightly for each gas independently from the kinetic diameters of gases.

In this study, mixed matrix membranes of conducting polymer, polypyrrole (PPy) and insulating polymer, hexafluorobisphenol A based poly(arylene ether ketone) (PAEK) were also prepared. It was observed that PAEK and PPy form a composite mixed matrix structure, which can function as permselective membrane. The effect of conducting polymer filler content was investigated with two different filler ratios. When comparing with the pure PAEK membranes, meaningful increases for both permeability and selectivity were obtained for some of the gases.

Key Words: Gas Separation, Dense Homogeneous Membrane, Mixed Matrix Membrane, Poly(arylene ether ketone), Conductive Polymers

ÖZ

POLİARİLENETERKETON MEMBRANLARIN VE POLİPİROLLÜ KARIŞIK YAPILI MEMBRANLARININ GAZ GEÇİRGENLİK ÖZELLİKLERİ

Mergen, Görkem

Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü

Tez Yöneticisi: Prof. Dr. Levent Toppare

Ortak Tez Yöneticisi: Prof. Dr. Levent Yılmaz

Temmuz 2003, 79 Sayfa

Endüstriyel gaz ayırımı için kullanılan sentetik membranların kullanılma olasılığı, bu teknolojinin avatanjları olan verimli enerji tüketimi, uygulamadaki kolaylığı ve düşük maliyeti sayesinde ilgi gören bir konu halini almıştır. Fakat daha geniş kullanım alanına sahip olması için, membran teknolojisi yüksek geçirgenlik ve taşınım seçicilikleri açısından hala geliştirilmesi gereken bir tekniktir.

İletken polimerler, yüksek gaz taşınım seçicilik özelliklerine sahip olmaları sebebiyle gaz ayırımı için yeni bir polimerik malzeme olarak ortaya çıkmıştır. Ancak düşük mekanik özellikleri yaygın kullanımını engellemektedir. Böyle bir problem ise araştırmacıları iletken polimerler ile yalıtkan polimerleri birlikte kullanarak karışık yapılı kompozit membranlar oluşturma fikrine götürmüştür.

Grubumuz tarafından yapılan önceki çalışmalarda iletken polimer olarak polipirol seçilmiş, farklı hazırlama teknikleri geliştirilmiş ve membran uygulamaları için optimize edilmiştir. Yine iletken polimere mekanik açıdan destek sağlayan polikarbonat yalıtkan polimeri kullanılarak iletken kompozit membranlar oluşturulmuştur. Bu çalışmada ise farklı bir polimer matrisi olaran poliarileneterketon endüstride önem taşıyan fiziksel özellikleri ve sıcaklığa olan direnci nedeniyle tercih edilmiş ve kullanılmıştır.

İlk olarak, bu polimerik materyalin gaz geçirgenliği özelliğini karakterize etmek amacıyla N_2, CH_4, Ar, H_2, CO_2 ve H_2 gazlarının geçirgenlik ölçümleri 25 °C den 85°C kadar değişen sıcaklık aralığında yapılmıştır. Ölçümler laboratuar boyutunda bir deney düzeneğinde, sabit hacim-değişken basınç yöntemi kullanılarak gerçekleştirilmiştir. Elde edilen geçirgenlik değerleriyle her gaza ait bu polimer matrisindeki geçirgenlik aktivasyon enerjileri hesaplanmıştır. Hesaplanan sonuçlar değerlendirildiğinde birbirinden çok da farklı olmayan geçirgenlik aktivasyon enerjileri ortaya çıkmıştır.

Bu çalışmada aynı zamanda iletken bir polimer olan polipirol (PPy) ve yalıtkan bir polimer olan hekzafloropolibisfenol esaslı poliarileneterketondan (PAEK) karışık yapılı membranlar hazırlanmıştır. PPy ve PAEK çiftinin çalışabilir karışık yapılı membranlar oluşturduğu gözlemlenmiştir. İletken polimerin geçirgenliğe olan etkisi iki ayrı komposizyonda incelenmiş, saf PAEK membranları ile kıyaslandığında hem geçirgenlikte hem de seçicilikte bazı gazlar için anlamlı artışlar saptanmıştır.

Anahtar Kelimeler: Gaz ayırımı, Yoğun Homojen Membranlar, Karışık Yapılı Membran, Poliarileneterketon, İletken Polimerler

To My Dear Family

ACKNOWLEDGMENTS

I wish to express my deepest gratitude to my supervisor, Prof. Dr. Levent Toppare for providing me with support, encouragement, and invaluable guidance.

I would like to show my appreciation to my co-supervisor Prof. Dr. Levent Yılmaz, for his precious suggestions, discussions, and support.

I also thank to the research team members for their friendship and support during my study; Selmiye Alkan, Ali Çırpan, Altan Gürsel, Yusuf Güner, Canan Biran, Özge Papilla and other teammates. I also would like to thank specially to Pelin Hacarlıoğlu and Değer Şen for their experimental and moral support.

I would like to thank my parents for their great support and patience during all my education and especially for their lifetime effort on me.

And to my little niece Serra, whenever things get unbearable, even a tiny thought of her made me feel better.

TABLE OF CONTENTS

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURES

NOMENCLATURE AND ABBREVIATIONS

D : diffusion coefficient

DSC : differential scanning calorimeter

dn /dt : molar flow rate

dP /dt : steady state pressure difference

E_d : activation energy of diffusion

E_p : activation energy of permeation

FFV : fractional free volume

H_s : heat of solution

J : flux of a gas through membrane

M : molecular weight of gas

P : permeability coefficient

p_h : high pressure side

p_l : low pressure side

PAEK : poly(arylene ether ketone)

PAEK(6FBisA) : hexafluorobisphenol A based poly(arylene ether ketone)

PANi : polyaniline

PC : polycarbonate

PPO : 2,6-dimethyl-1,4-phenylene oxide

PPy	: polypyrrole
PTSA	: p-toluene sulfonic acid
R	: ideal gas constant
S	: solubility coefficient
SEM	: scanning electron microscopy
T_g	: glass transition
TGA	: thermal gravimetry analyzer
TMPC	: tetramethyl polycarbonate
TMHFPC	: tetramethylhexafluoro polycarbonate
6FDA-DAF	: hexafluorodianhydride with 2,7 fluorediamine
6FDA-IPDA	: hexafluorodianhydride with isopropylidenedianiline
6FPPy-6FPBA	: fluorine containing poly(arylene ether) with 2,6 bis(trifluoromethylphenylene)pyridine
6FPT-BPA	: poly(arylene ether) with 2,5 bis(3-trifluoromethylphenylene)thiophene
ΔP	: pressure difference
V	: dead volume
μ	: carrier mobility
α_{ij}	: ideal separation factor
δ	: thickness of membrane
ρ	: density of permeate gas

CHAPTER 1

INTRODUCTION

Through the last 25 years, the membrane technology gained importance as one of the industrial technological developments. The separation of gas mixtures appeared to be one of these economical and often limited industrial applications.

Membrane based gas separation is a novel technique which introduced commercially in 1970's, providing energy efficiency, environmental and product quality advantages over conventional technologies. Synthetic membranes are thin, solid phase barriers that allow preferential passage of certain substances under the influence of a driving force. Membrane separation occurs because of differences in size, shape, chemical properties or electrical charge of substances [1].

Membrane based gas separations compete with cryogenic separations and also wide range of absorption and adsorption processes like pressure swing adsorption and amine treatment. An obvious advantage of gas membrane is their simplicity of operation and installation. In many applications, membranes have a lower capital outlay and require no utilities unless a compressor is needed [2]. Since they are modular and have a capacity to be added to an existing plant, membrane processes are very flexible. They are generally weight and space efficient, which are important in transportation or offshore platform applications. Their environmental impact is low because they contain no toxic liquids and are compact in size. Rising energy costs and environmental concerns in recent years have forced both the industrial and governmental sectors to increase their efforts for development of energy efficient and clean separation process. One apparent answer to these processing needs is the use of membranes [3].

The first large-scale use of membranes to separate gases was in the gaseous diffusion process for separation of uranium isotope. This process was first developed in the U.S. in the 1940's and utilized microporous membrane, as the separation barriers. The first large-scale gas separation plant based on polymeric membranes was installed by the Monsanto Co. in 1977 for the recovery of H_2 from an industrial gas stream [4].

Historically, membrane separation of gases has been limited to some extent by relatively low fluxes and selectivities. However, recent developments in membrane technology for gas separation have been made to correct these long standing problems. New membrane materials, novel methods for membrane fabrication, consideration of transport processes and imaginative ideas in engineering design are all contributing to the commercialization of membrane processes technology [5].

Intensive investigation of gas separation characteristics of polymeric membranes in 1980's resulted in rapid improvements in their properties and speculations on the limits of performance of such membranes [6]. Due to the more restricted segmental motions in glassy polymers, these materials offer enhanced selectivity of components according to their diffusion characteristics as compared to rubbery polymers. Since, glassy polymers are inherently more size and shape selective than rubbery materials, they are commonly used as the selective layer in gas separation membranes [7]. In early 1990's, an upper limit of performance for polymeric membranes was noted for the industrially important separation of oxygen from nitrogen [8]. This observation was based on a comprehensive review of the gas transport properties of more than 300 conventional polymeric materials. Significant progress in membrane separation technology depends on the explanation of mechanism for gas transport. An insufficient understanding of the relationships between the chemical structure of a polymer and its gas transport properties may prevent this progress.

Simple parameters of polymer molecular structure such as T_g and FFV (fractional free volume) should be used to understand much of data related to the effects of structural changes on the resultant permeability and permselectivity properties of given family of polymers. Such studies are the first steps toward identification of chain structural characteristics that are suited for operations at elevated temperatures (i.e. increased productivity without a dramatic loss in selectivity) [10]. For this study, to characterize the permeability behavior, hexafluorobisphenol A based poly(arylene ether ketone) was selected due to its physical properties and temperature resistance which has importance for industrial applications.

As membrane technology matures, the question of which area to expand into also arises. Use of polymeric membranes in applications that operate at temperatures of above 100ºC is one option. In industry, gas separation at high operating temperature could be necessary for in-situ treatment of gas mixtures. In many separation processes, gas separation membranes at high temperatures should separate gas mixtures exiting from any unit at high temperatures without needing any cooling process and energy loss. On the other hand, polymeric materials are not well suited for such applications due to their low mechanical strength and separating ability at high temperatures. Over the past decade, a number of polymeric materials with improved thermal stability have been reported. The ultimate operation temperature of polymer is difficult to predict from thermal analysis, whereas, the polymer's glass transition, T_g has been widely used as an estimate of this value [9].

Attractive industrial applications using membranes may be currently overlooked due to the lack of data concerning the effect of temperature on gas separations. Simpler and more energy efficient processing schemes eliminating cooling of mixed gas streams prior to separation are of particular interest.

Characterization of temperature dependency of gas transport properties of membranes is very important. This characterization may help exploring the high temperature operations in gas separation membranes that accompanies undesirable changes in the membrane performance. In addition, characterization of membrane itself and transport mechanism through it are also very important. Different membrane preparation techniques can form different inner structures affecting the membrane performance and high temperature gas permeation experiment may enhance and reveal these differences.

As previously mentioned, over the last 25 years, the gas separation properties of many polymers have been measured and substantial research effort in industrial, government and university research laboratories has resulted in polymers that are more permeable and selective than the first generation polymers [11]. The attraction of using conducting polymers as membrane materials are their inherent conductivity and their reversible redox, electro-active properties. Thus, they present a new generation of membrane materials with tailored molecular architecture for specific selectivity[6]. Dopable conjugated polymers of which conducting polymers constitute a subgroup, form a relatively new class of polymeric materials that have been studied extensively for their electrical properties since the first doping experiments were reported on polyacetylene in 1977. Although the features that predispose these polymers to being conductive may still be important, their electrical conductivity plays only an indirect role. The conducting polymers may have good separation characteristics due to their concentration of fixed sites in their structure showing exceptional gas transport selectivity and their potential for easy synthesis of these films. The doping process that makes these materials conductive allows precise changes in morphology [12]. These are redox active polymers that can exist in a fully reduced, a fully oxidized, or a partially oxidized form and can show very high gas transport selectivities dependent on their microstructure.

Although conducting polymers offer a number of important advantages, polypyrrole and its analogs are hard and brittle materials. These undesirable mechanical characteristics restrict the technological applications of these polymers

[13]. Preliminary work has shown that gas separation with polypyrrole is very promising. Another possibility to construct polypyrrole-based membranes is to combine them with a second conventional substrate to improve performance. Thus PPy films have been deposited on alumina or polycarbonate substrate to form durable permselective membranes for gas and liquid separation [14].

In this study, our aim was to study both pure hexafluorobisphenol A based poly(arylene ether ketone) (PAEK) and PPy-PAEK mixed matrix membranes. For this purpose, we investigated the temperature dependency of PAEK membrane performance in gas separation membrane processes and try to understand the permeation mechanism of gas molecules through this polymer matrix. PPy-PAEK mixed matrix membranes were prepared to combine the good membrane characteristics of conducting polymers with good mechanical properties of insulating glassy polymers.

CHAPTER 2

LITERATURE SURVEY

2.1 Membrane Morphologies For Gas Separation

A membrane will separate gases only if some components pass through the membrane more rapidly than others do. This requirement places its constraints on the structure of the membrane's separating layer in other words, the morphology of the membrane is the criterion which may determine the separation mechanism.

The simplest morphology is dense homogeneous polymeric membrane, which is composed of a nonporous dense single polymer layer, homogeneous in all directions. The permeabilities of virtually all common gases were thoroughly explored by employing mostly dense homogeneous physical membrane structure to new polymer chemistries [15]. This structure is still the most suitable morphology to investigate the effect of new polymer chemistries and chemical modifications and also serves as a standard when new morphologies are explored.

A breakthrough to industrial applications was the development of asymmetric membranes. These are characterized by a non-uniform structure compromising a dense selective active top layer or skin supported by a porous sub-layer of the same material. The resistance to mass transfer is determined largely or completely by the thin top layer [15].

It is also possible to obtain composite membranes which are in fact skinned asymmetric membranes. However, in these membranes, top layer and sub layer originate from different materials and each layer can be optimized independently.

The latest emerging composite membrane morphology is the mixed matrix one where interpenetrating matrices of different material is produced either by blending or by in-situ polymerization instead of forming separate layers. The most common reason for adding fillers, especially high aspect ratio fillers, to polymers is to improve gas permeation performances while increasing their stiffness, thermal stability, electrical conductivity and optical effects [16].

2.2 Transport Mechanisms for Gas Separation Membranes

As mentioned in the previous section, separation takes place according to the morphology of the membrane which is based on different separation mechanisms. If the membrane contains pores large enough to allow convective flow, separation will not occur. If the size of the pores is smaller than the mean free path of the gas molecules, then convective flow is replaced by Knudsen diffusion. In this case gas molecules interact with the pore walls much more frequently than with one another and low molecular weight gases are able to diffuse more rapidly than heavier one thus, separation occurs [17]. In the limit of zero permeate pressure, the difference in transport rates of two components is inversely proportional to the square root of the ratio of their molecular weights.

If the pores are small enough, large molecules are unable to pass through them and are excluded by the membrane. This molecular sieving is potentially useful in separating molecules of different sizes [17].

The membranes currently used in most commercial applications are solution-diffusion membranes. These membranes are so named since transportation of gas molecules in these membranes is mainly achieved by the solution and diffusion mechanism. Transport occurs when gas molecules dissolve in the membrane and then diffuse across it. Chemical composition of the polymer that forms the selective membrane layer, steric relationships in repeat units of the selective polymer, morphology of the membrane's separating layer, the overall membrane structure, including structural relationships between the separating layer and the rest of the membrane are the factors which influence the ultimate performance of polymeric solution-diffusion membranes. Briefly, the gas dissolves at the membrane surface and diffuses through by a series of activated steps. As the last step, the gas evaporates at the low pressure side.

The solution diffusion mechanism involves molecular scale interactions of the permeating gas with the membrane polymer; thus it can be expressed in terms of the transport and sorption coefficients for the individual polymer and gas. A more common way of expressing this relation is:

$$P = D * S \qquad (2.2.1)$$

The quantity S, solubility is thermodynamic in nature and is affected by polymer-penetrant interactions as well as excess interchain gaps in glassy polymers. The average diffusion coefficient D is kinetic in nature and largely determined by polymer-penetrant dynamics.

Expressing performance of a membrane, required descriptions are formulized.

The flux (J) of gas through membrane is given by:

$$J = P\,(P_h - P_l) / \delta \qquad (2.2.2)$$

where P is permeability, P_h and P_l are the partial pressures of the gas on the feed side and the permeate side respectively and δ is the thickness of the membrane.

For single gas measurements, ideal gas selectivities are found by rationing the individual permeabilities of two gases, i and j respectively.

$$\alpha_{ij} = P_i / P_j \qquad (2.2.3)$$

In order to obtain the real gas selectivities, the performance for binary gas mixtures should be performed. The ideal separation factors are obtained by assuming the ineffectiveness of composition variation on the separation performance of polymeric membranes.

2.3 Polymer Selection for Gas Separation Membranes

Synthetic membranes are thin, solid-phase barriers that allow preferential passage of certain substances under the influence of a driving force such as partial pressure gradient for gas separation. Polymers provide a range of properties important for separations and modifying them can improve membrane selectivity. A material with a high glass-transition temperature, high melting point and high crystallinity is preferred. Glassy polymers (below their T_g) have stiffer polymer backbones and therefore, let smaller molecules such as hydrogen and helium pass more quickly; larger molecules such as hydrocarbons permeate the membrane more slowly. Rubbery polymers (above T_g) in contrast allow the hydrocarbons to permeate more readily than the smaller gas molecules [18].

Gas molecules permeate through a rubbery polymer quickly because the binding force between molecular segments of the polymer is not strong and segments can move relatively easily to open a channel through which even large molecules can pass. Due to the more restricted segmental motions in glassy polymers, these materials offer enhanced mobility selectivity as compared to rubbery polymers. The size of the molecule and the diffusion coefficient are more important for the transport in glassy polymers.

Volatile organic compounds (VOCs) which have a strong affinity (high solubility) for polymeric materials permeate a rubbery polymeric membrane faster than the much smaller oxygen and nitrogen molecules. As hydrogen molecules are the smallest (high diffusion coefficient), membranes prepared from glassy polymers are used effectively for hydrogen separation. Similarly, in CO_2-CH_4 separation CO_2 permeates through glassy membranes much faster than methane partly because a CO_2 molecule has slightly smaller kinetic diameter than a CH_4 molecule and because the polymeric materials have a strong affinity to CO_2 [18].

Although considerable data and general correlations relating structure and permeability exist [17], there are no truly quantitative relationships to guide detailed structure–permeability optimization. Fortunately, qualitative rules have emerged that date back to the pioneers Hoehn and his colleagues at Dupont in the 1970's[17]. They simply stated that changing the structure within a family of polymers inhibiting intersegmental packing, while simultaneously hindering the backbone mobility, tends to produce a desirable tradeoff between productivity and permselectivity. Currently, this is the most reliable guide for understanding structure-mobility studies of a given family of polymers (polycarbonates, polysulfones, polyimides,etc.) [19].

A rather general tradeoff relation has been recognized between permeability and selectivity: Polymers that are more permeable are generally less selective and vice versa [20]. On the basis of an exhaustive literature survey, Robeson [20,21] quantified this notion by plotting the available data, which presents hydrogen and oxygen permeability coefficients with O_2 / N_2 and H_2 / N_2 separation factors for many polymers. Materials with the best performance would be in the upper right hand corner of this figure. However, materials with permeability/selectivity combinations above and to the right of the line drawn in this figure are exceptionally rare. This line defines the so-called "upper bound" combinations of permeability and selectivity of known polymer membrane materials for this particular gas pair. Lines such as the one shown in Figure 2.3.a and Figure 2.3.b. were constructed on an empirical basis for many gas pairs using published permeability and selectivity data. Robeson also noted the difference between the kinetic diameters of the penetrant molecules and suggested that the slope of the upper bound is a natural consequence of the strong size-sieving nature of the stiff chain glassy polymeric materials whose properties generally define the upper bound.

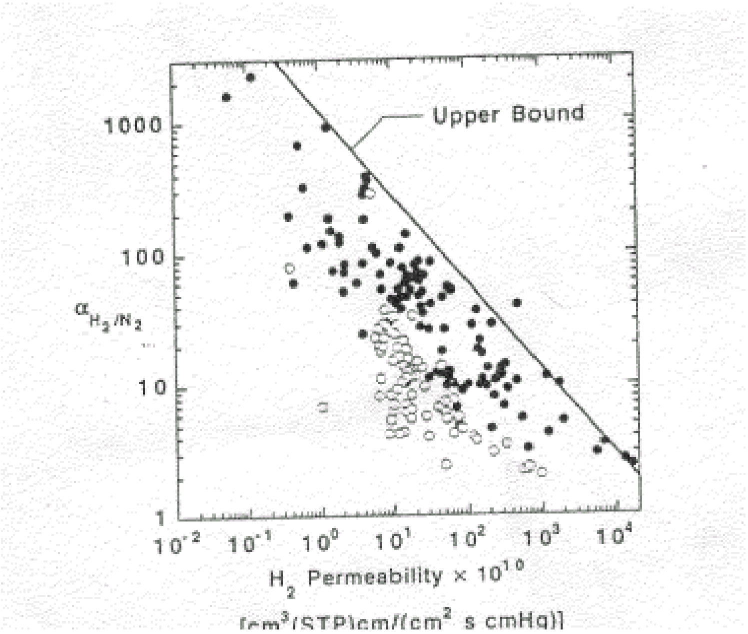


Figure 2.3.a. Relationship between hydrogen permeability and H_2/N_2 selectivity for rubbery (O) and glassy (●) polymers and the empirical upper bound relation [20]

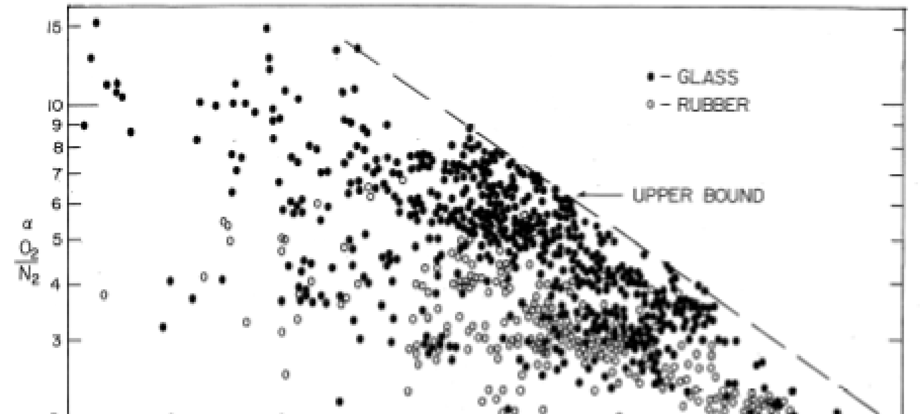


Figure 2.3.b. Relationship between hydrogen permeability and O_2/N_2 selectivity for rubbery (O) and glassy (●) polymers and the emprical upper bound relation [21]

A fundamental theory is provided by Freeman [11] for the above observation and according to this simple theory, there is no influence of the polymer structure on the slope of the upper bound. If this is true, then the slopes of the upper bound lines are unlikely to change with further polymer development efforts. In contrast, this theory contains variables to improve permeability and selectivity, either through solubility selectivity enhancement or increasing chain stiffness while increasing interchain spacing. Increasing interchain separation to increase permeability without sacrificing selectivity should only be effective as long as the interchain separation is not so large that penetrant diffusion coefficients are no longer governed by thermally stimulated polymer segmental motions. To achieve still higher selectivity/permeability combinations, materials that do not obey these simple rules would be required and this type of materials may already exist. Simultaneous chain stiffness and the increase in the interchain separation can be used to systematically improve separation performance until the interchain separation becomes large enough that the polymer segmental motion no longer governs penetrant diffusion. Poly(1-trimethylsilyl-1-propyne), the most permeable polymer known, exhibits many permeation characteristics similar to nano-porous materials. Also, polymers with other unusual properties such as conductivity may be exceptions and should be investigated and conductive polymers such as polypyrrole, polyaniline are some examples for these.

Several families of glassy polymers display striking properties for application as gas separation membranes. Polyimides, polyesters, polycarbonates and polyetherketones are some of these families which show high permeabilities and selectivities [18].

Many factors related to the chemical structure of polymer affect the membrane performance. Structure property relationship has been reported for many aromatic polymers comprised of aromatic groups in main chain with various linking groups and aromatic substitutions [21]. A simple concept is useful for understanding much of the data relating the effects of structural changes on the resultant permeability and permselectivity properties of a given family of polymers.

Hoehn [23] suggests that, it is desirable to do two things simultaneously when changing the structure within a family of polymers: Inhibition of intersegmental packing while simultaneously hindering the backbone mobility. Inhibitions to intersegmantal packing are reflected by an increase in the fractional free volume (FFV) of the polymer matrix. The inhibition of segmental mobility is reflected in an increase in the glass transition temperature. Various means can be used to inhibit motion; including intrasegmental steric effects, polar substituent groups, and intersegmental steric effects [10].

The effect of polymer structure on gas permeation behavior is of interest because of the need for improved barrier materials and gas separation membranes. In the former area, the absolute permeation rate is the primary issue, whereas in the latter selectivity of transport for different species is also important. Both are governed by the polymer segmental motions, cohesion and packing whose effects are most dramatic in the glassy state due to its low intrasegmental mobility and long relaxation times. The possibilities have been convincingly demonstrated in several recent studies where polymer molecular structure has been systematically varied within different classes of materials [3,8,24,25].

Alcock et al [26] in 1992, studied the change in permeability and selectivity as a function of side groups, free volume, gas pressure and glass transition temperature (T_g) by means of a series of poly (organophosphazane)s. As the incorporation of bulky phenyl groups attached to silicon increased, the permeability of the membrane to all of the gases decreased. However, polymers with bulky side units were expected to show high O_2 permeability values. This behavior was explained by an aggregated membrane structure. Also, it was concluded that, an increase in polymer density resulted in a decrease in gas permeation with higher incorporation of phenyl side groups. On the other hand, an increase in polymer molecular weight caused both O_2 permeability and selectivity to increase and then, gradually leveled off. Stern et al. [26] in 1987, studied silicon polymers considering the large variety of functional groups that can be substituted in the side and backbone chains to observe the relationship between polymer structure and permeability. This study showed that, the substitution of bulkier functional groups in the side and backbone chains of silicon polymers decreased the gas permeabilities of these polymers substantially by means of a decrease in penetrant diffusivities. To support their hypothesis, again, Stern et al. [27] in 1989 studied the permeability of nine different polyimide membranes. They tried to identify the structural factors which would cause synthesis of new polymeric membranes to have both high permeability and selectivity. One of these factors was found as chain stiffness which appears to be a requirement for high mobility selectivity. Other important factor was the main chain packing density which controlling the diffusivity of penetrant molecules. It was concluded that, polymers with very rigid backbones and a high packing density exhibited a high selectivity but, a very low diffusivity and hence also, a very low permeability. But, by the substitution of side chains of appropriate bulkiness that can serve as interchain spacers without greatly reducing the polymer volume, the diffusivity of penetrant gases increased without a significant loss in selectivity.

A number of methods have been proposed for correlating permeability coefficients to different structural or physical properties of polymers and penetrant gases [28-31]. Such correlations can be used, if sufficiently accurate, to predict values of permeability coefficients for new polymers. The correlations are generally applicable under conditions where the polymers are not significantly plasticized define structure-permeability relationships. They observed that, there were direct correlations between the measured properties of polymer density and interchain d-spacing and the oxygen permeability value of the polymer. In addition, they also observed that, polyimides with unsymmetrical substituents exhibit the highest selectivity values due to an increase in interchain attraction due to a dipole effect.

In the same manner, Hirayama et al [29] in 1996, studied 32 kinds of polyimide films to investigate how the variation of polymer-structure would influence gas diffusivity and to correlate gas diffusivities with some parameters depending on physical properties of polymers. This study showed that, it might not be proper to explain gas diffusion only by total free spaces or mean segmental distance. Especially, in case of glassy polymers such as polyimides constructed of substituents including halogens, it may be needed to consider mobility of glassy polymers reflecting interaction of polar group in side chain. After this study, the same research group [30] investigated relations of apparent diffusion coefficients and physical parameters with a mobility of segments in order to clarify relation between the gas diffusivities and the polymer structure. After that, it was clarified that, gas molecules in the glassy polymers may diffuse easily with an increase of the mobility of segments and that the estimation of gas diffusivities may be possible by the use of a factor CED (Cohesive Energy Density).

Lianda et al [31] in 1990, studied the permeability data of 60 homopolymers to relate gas permeability with gas molecule diameters and two polymer structure parameters, cohesive energy density and free volume, without taking into account such factors as crystallinity, orientation and rubbery or glassy state. A good relationship was found between log P and the ratio of (V_f / E_{coh}) of polymers and between both the intercepts and the slopes of the lines on the log P vs. (V_f / E_{coh}) plots and the square of gas molecule diameters. Therefore, the permeabilities of all non-swelling gases through almost all the polymeric membranes can be estimated from this relationship.

A very substantial amount of the solution-diffusion and permeation of many gases and vapors in a variety of rubbery and glassy polymers was already available over 10 years ago [4,32]. Yet, the relationships between the chemical structure of polymers and their gas permeability and selectivity were only poorly understood.

This was due to the fact that, pertinent measurements were seldom made with polymers whose chemical structure were systematically altered by the substitution of selected functional groups in their backbone or side chains. It is only recent years that, the structure/permeability/selectivity relationships of polymers have become the object of systematic studies [4,32]. Further, significant progress in membrane separation technologies will be possible only through the synthesis of new polymeric membranes that exhibit both a high selectivity for specific gases and a high permeability.

2.3.1 Poly(ether ketone)s

The method most frequently utilized for the preparation of poly(arylene ether)s is aromatic nucleophilic substitution of fluorides or chlorides from aromatic bishalides and bisphenolates. The aromatic bis(arylhalide)s are activated toward nucleophilic substitution by the carbonyl or sulfone groups. Unless carefully designed, however, poly(ether ether ketone)s (PEEKs) are often exhibit low solubility in common organic solvents at high temperatures. Therefore, a preparation of soluble and/or processable poly(arylene ether)s without sacrifying their desirable properties has been of major research interest [33]. The concepts for structural modifications such as the introduction of flexible bridging linkages or meta-oriented phenylene rings into the polymer backbone and incorporation of methyl substitute or bulky substituents along the polymer chain have been used to enhance the solubility and the processibility. Also several researchers reported [34, 35] that introduction of hexafluoroisopropylidene groups between rigid phenylene rings improves the solubility. PEKs are partially crystalline (approximately 35%) PEEK and PEK respectively have glass transition temperatures of 143 and 165 ºC and melting temperatures of 334 and 365 ºC. Both of them show excellent resistance to a wide range of aqueous and organic environments [33].

Poly(arylene ether)s are well accepted as a high performance engineering thermoplastics and offer excellent combination of chemical, physical and mechanical properties at ambient and elevated temperatures. ICI’s VictrexTM, poly(ether sulfone) (PES), and semicrystalline poly(etherether ketone) VictrexTM (PEEK), Amoco’s UdelTM poly(sulfone) and KadelTM poly(ketone) are commercially available and important high performance engineering polymers. They are used in a variety of applications such as coatings, adhesives, matrix resins for advanced composites, toughening agents and ultrafiltration membranes [34-35]

Due to these advantages, poly(etherketones) are being synthesized to obtain superior qualifications.

In 1992 Fukawa and co-workers [36] synthesized six different type of poly(etherketone) changing the structure by increasing the number of carbonyl group along the chain. They compared those polymers with a new type including dibenzofuran group and observed an improving trend from the low to more ketone content. They found that dibenzofuran containing PEK's show much better thermal properties. PEKBK's have T_g value of 220 ºC where as the upper T_g of other new synthesized PEKs were 159 ºC beside this excellent thermal stability dibenzofuran type polyether ketone PEKBK amorphous polymer showed good mechanical properties.

Bourgeois et. al. [37] worked on the block copolymers containing polyethersulfone (PAES) and poly(aryletherketone) (PAEK). The resulting triblock PAEK-PAES-PAEK was no more soluble than parent PAEK material however, it seemed to be promising as the block copolymers fulfill the requirements; a T_g above 200 ºC together with a T_m around 350 ºC which also satisfies engineering requirements for a high performance composite matrix.

Mercer and his coworkers [38] found that activated aryl fluorides in 2-chloro-7-fluoro benzonitrile are selectivity displaced by phenoxides to yield 3-chloro-2-cyanophenyl ethers as the exclusive products. Utilizing this selectivity several new, high molecular weight, soluble poly(aryletheramide) and poly(aryletherketone) alternating copolymer containing pendent cyano groups were prepared. The T_g's of the copolymers ranged from 160-262 ºC. All were processable from solution to yield transparent flexible films.

Same group of scientists [39] prepared a series of fluorinated polyetherketones containing perfluoroaryl moieties by solution condensation polymerization. They demonstrated that the fluoro groups in para position of decafluorobenzophenone are preferentially displaced by the alkali metal salt of a bisphenol to yield fluorinated PEK's containing perfluoroaryl moieties. All four fluorinated poly(etherketones) were soluble in polar aprotic solvents; cast into flexible creasable films and high temperature resistant. They declared that high T_g fluorinated aromatic polyetherketones can be useful for industrial application.

In 1997 Selampinar and her coworkers [40] studied on a novel poly(arylene ether ketone) and its conducting composites with PPy. PAEK designed and synthesized due to obtain a polymer with distinctive mechanical properties. Fluorine substituents hexafluoroisopropylidene group was positioned on the repeating unit to obtain high solubity and thermal stability. Synthesized polymer displayed T_g at 185ºC and a weight loss of 5 % at 520 ºC. It was soluble in chloroform and a flexible solid structure. Electrochemical composite of this new material PAEK and PPy, besides good environmental stability, thermal, mechanical properties and flexibility, also gained conductivity. These promising advantages of this material brought the idea of using it as a gas separation membrane.

2.3.1.1 Gas Transport Properties of Poly(ether ketone)s

One of the key objectives in gas separation research continues to be improving permeabilities and selectivities simultaneously without sacrifying the other useful properties. For example in oxygen enrichment, new materials are needed with enhanced flux/selectivity at elevated temperatures [41] and poly(ether ketone)s are investigated as an alternative gas separation membrane polymer.

Mohr and Paul et al [42] studied gas sorption and transport properties of a series of poly(aryl ether ketone)s. In these series, the isopropylindene groups, $-C(CH_3)_2-$, in the backbone systematically replaced with a hexafluoroisopropyrilidene group ($-C(CF_3)_2-$). Besides dynamic mechanical analysis and differential scanning calorimetric analysis to display the change in stiffness, CH_4 and CO_2 sorption measurements were made to examine the solubility and diffusivity coefficients. They reported that as ($-C(CF_3)_2-$) units replaces with isopropylindene groups diffusivity increases which accounts increase in permeability. Along with increase in permeability was an increase in selectivity for gas pairs like He/CH_4 and CO_2/CH_4.

In 1993, Paul, Aitken and Mohanty [43] reported their research about the gas transport properties of poly(arylether bissulfone) based on bisphenol A (PBSF) and poly(arylether bisketone) based on bisphenol A (PBK). They compared with polysulfone and polycarbonate also based on bisphenol A to determine the effect of long rigid bisketone and bissulfone groups. Bulkier sulfone groups increases the free volume and T_g more than ketone group, resulting an increase in solubility and diffusivity coefficients which contribute to a higher permeability.

Maier and coworkers [44] worked on a series of poly(ether ketone)s containing indan groups. The effects of structural variations on permeability coefficients and selectivities for the gas pairs H_2/N_2, CO_2/N_2, H_2/O_2, CO_2/O_2 and H_2/CO_2 were discussed. A specific chain segment was identified tentatively, which controls the selectivity. This segment consists of a sequence of flexibly linked phenyl rings and were connected by the bulky and immobile indan groups.

Wang et al [45] presented the results from gas permeability studies on a novel poly(arylene ether ketone)s in 1997. Poly(arylene ether ketone)s containing 2,2'- and 3,3'-dibenzoylbiphenyl (DBBP) moieties were characterized to study the effect of biphenyl substitution on gas transport properties. Based on their work in correlation with the literature results, the 3,3'-DBBP polymers showed the lowest permeabilities among the DBBP containing poly(arylene ether ketones). They reported that low permeabilities were due to more efficiently packed chains brought on by the greater flexibility of the backbone, compared to the other polymers studied. Dynamic mechanical analysis confirmed the higher barriers to rotation which are believed to be responsible for 2,2'-DBBP polymers having similar selectivities compared to 3,3'-DBBP polymers.

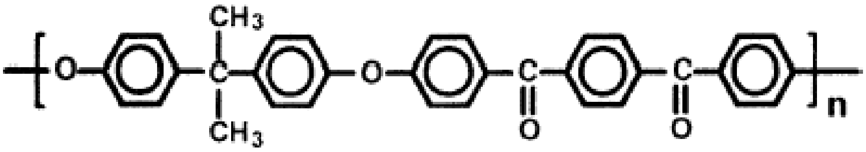
In a recent work of Zhi-Kang Xu, Jürgen Springer and their coworkers [46] gas transport and separation properties of H_2 CO_2, N_2, and CH_4 were studied for four novel poly(arylene ether)s (PAEs) membranes, two containing the 2,6-bis(trifluoromethylphenylene)pyridine unit (6FPPy series) and others containing 2,5-bis(3-trifluoromethylphenylene)thiophene unit (6FPT series) in the backbone. It was found that the introduction of $-CF_3$ groups into bisphenol unit increases the gas permeabilities and decreases slightly the selectivities for both series of membranes. The gas permeability coefficients of 6FPPy membranes are higher than those of 6FPT membranes while their selectivities are comparable. These results were discussed based on the gas diffusion and solubility in the membranes and ascribed to the polymer structure. The effect of temperature on the gas transport properties of these membranes was measured and the corresponding activation energies for gas permeation and diffusion were calculated.

Xin-Gui Li, Jürgen Springer and their coworkers [47] prepared a homogenous dense membrane of bisphenol A poly(ether ether ketone ketone) (PEEKK) by solution casting technique with chloroform as solvent. The permeability, diffusivity, solubility and their selectivities of O_2, N_2, CO_2, CH_4 and H_2 through membrane were measured by a change in operating temperature and upstream pressure. Solubility of five gases in the PEEKK membrane increases with decreasing temperature. The solubility selectivity in the PEEKK membrane almost remained constant with changing the upstream pressure. The highest O_2/N_2, CO_2/CH_4, and H_2/N_2 selectivity coefficients were respectively equal to 7.06, 23.1, and 106.1.

In Table 2.3.2 [47] permeability and selectivity values of some poly(ether ketone)s in the literature are listed. Since different molecular structures are under consideration, even though all have the same ketone and ether structural properties, different values are obtained by different research groups. 10 types of ether ketone polymers including PEEKKs, poly(ether ether ketone)s, and poly(ether ketone ketone)s are listed. It is seen that wholly aromatic poly(ether ketone ketone)s exhibits the highest O_2/N_2 and H_2/N_2 selectivities in 10 polymers but the lowest O_2 and H_2 permeability. Tetramethylbiphenyl unit-containing poly(ether ketone ketone) has the highest O_2 and CO_2 permeability, but its O_2/N_2 and H_2/N_2 selectivities are low compared with most of other polymers listed in Table 2.3.2.

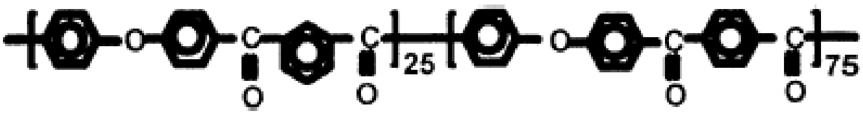
Table 2.3.2 : Comparison of gas transport in various aromatic poly(ether ketone) membranes [47]

(1)

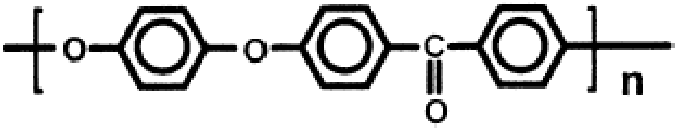


(2)

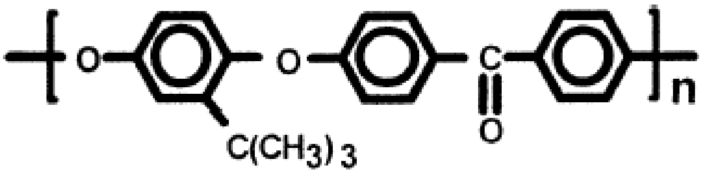
(3)



(4)



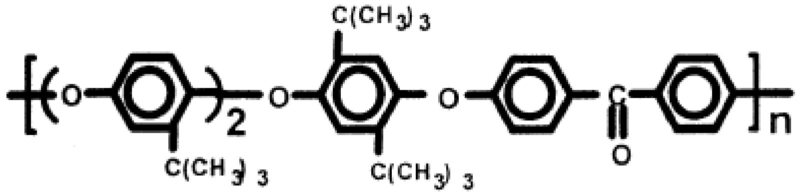
(5)



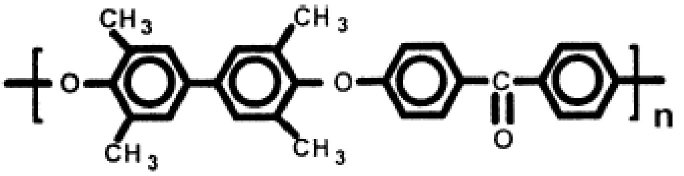
Polymer No:	**Permeability (Barrers)**					**Selectivity**		
	O_2	CO_2	H_2	CH_4	N_2	O_2/N_2	CO_2/CH_4	H_2/N_2
(1) (at 25 °C)	0.47	1.81	7.31	0.06	0.06	8.3	32	130
(2) (at 35 °C)	0.61	2.18	9.38	0.08	0.09	6.86	26	103
(3) (at 30 °C)	0.17	-	2.90	-	0.02	8.3	-	140
(4) (at 35 °C)	0.26	0.96	-	0.03	-	6.5	31	-
(5) (at 35 °C)	1.39	4.65	-	0.22	-	6.4	21	-

Table 2.3.2 ***(Continued)*** Comparison of gas transport in various aromatic poly(ether ketone) membranes [47]

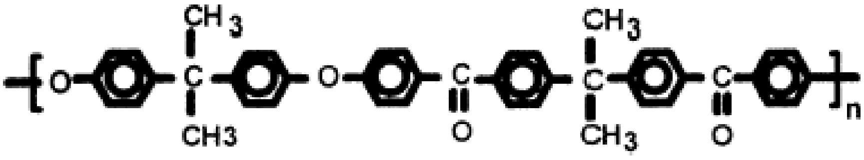
(6)



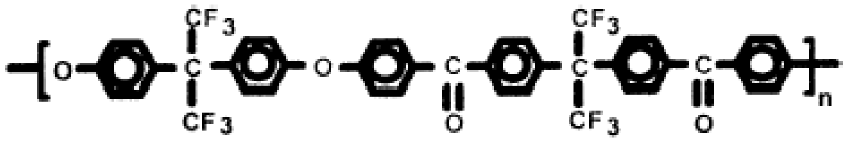
(7)



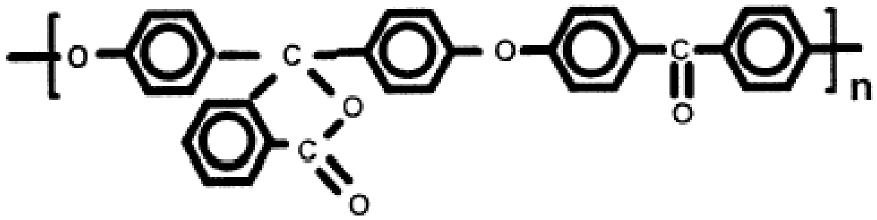
(8)



(9)



(10)



Polymer No:		**Permeability (Barrers)**					**Selectivity**		
		O_2	CO_2	H_2	CH_4	N_2	O_2/N_2	CO_2/CH_4	H_2/N_2
(6)	(at 35 ºC)	2.19	6.91	-	0.38	-	6.3	18	-
(7)	(at 35 ºC)	4.76	19.4	-	1.02	-	4.9	19	-
(8)	(at 35 ºC)	1.1	4.6	12.4	0.23	0.21	5.7	20	59
(9)	(at 35 ºC)	3.7	12.9	31.4	0.54	0.77	4.8	24	41
(10)	(at 25 ºC)	1.0	2.7	5.0	0.08	0.16	5.7	32	32

2.3.2 Effect of Operational Temperature

According to the solution diffusion theory, which is thought to be valid for homogeneous membrane morphology, permeation is a solution-diffusion process that can be described in terms of the sorption and transport coefficients for the individual polymer and gas. Therefore, the permeability coefficient can be expressed as a product of a diffusion coefficient and a solubility coefficient.

The solubility coefficient is a thermodynamic term that is determined by the condensibility of the penetrant and the polymer-penetrant interactions. The diffusion coefficient is a kinetic term related to the amount of energy necessary for the penetrant to execute a diffusive jump through the polymer matrix and to the intensity of the segmental packing [48].

Within a temperature range without any significant thermal transitions of the polymer, the temperature dependence of solubility and diffusion coefficients, and consequently the permeability coefficient can be described by the expressions below respectively,

$$S = S_o \operatorname{Exp}(-H_s/RT) \tag{2.3.1}$$

$$D = D_o \operatorname{Exp}(-E_d/RT) \tag{2.3.2}$$

$$P = P_o \operatorname{Exp}(-E_p/RT) \tag{2.3.3}$$

where H_s is defined as the heat of sorption, E_d is defined as the activation energy for diffusion and E_p is defined as the activation energy for permeation which is simply the sum of the activation energy for diffusion and the heat of sorption. [9]. Depending on domination of these coefficients in the temperature dependency of the permeability, one can get an idea about the permeation mechanism of gas molecules in polymers. The effect of temperature on the transport and sorption behaviors of glassy polymers has not been well characterized, even though changes in operating temperature are known to affect the performance of a membrane material significantly [24].

A large amount of data exists for gas transport in polymer films at constant temperatures near 25 or 35 ºC. Even though it is a well known fact that physical properties of polymers are affected strongly by temperature changes, the transport behavior of polymeric materials as a function of temperature have been studied by only a few research groups In Table 2.4.1, literature studies on temperature dependency of permeabilities of polymeric membranes are summarized. According to these studies, for many polymeric materials, a slope discontinuity near T_g is observed in the Arrhenius plot of permeability versus temperature as well as negative permeation activation energies for Teflon AF 2400. It can be concluded that, a small change in operating temperature can affect significantly the productivity and selectivity of the membrane.

Costello and Koros [24] in 1994, studied the temperature dependence of permselectivity of polycarbonate membranes up to 200 ºC. The activation energies for permeation and diffusion and heats of sorption for each gas in the three polycarbonates; bisphenol-A polycarbonate (PC), tetramethyl polycarbonate (TMPC) and tetrarmethylhexaflouro polycarbonate (TMHFPC) were also reported. This study has shown that, rigid backbone polymers with few or hindered mobile linkages were less sensitive to changes in operating temperature and would therefore be favorable candidates for novel gas separations at elevated temperatures. Kim, Koros and Husk [49], measured the gas permeation rate of two hexafluoro-substituted aromatic polyimides to investigate the temperature dependency of gas transport properties for various gas pairs. These polyimides have exceptionally high permeabilities and permselectivities as compared to typical glassy polymers used in gas separation membrane applications. It was observed in this study that, the temperature dependency of the permeabilities of all penetrants in these polyimides also was smaller than in other standard glassy polymers having backbones that are more flexible. It was concluded that, the differences in activation energies between larger and smaller penetrants in these rigid structures, were more extreme than in standard glassy polymers, thereby, causing a stronger temperature dependency of permselectivity than more flexible backbone glassy polymers.

Table 2.4.1 Studies About Temperature Dependency of Polymeric Membranes

Polymer	Temperature Range	[Ref]	Remarks
32 kinds of polyamides	35-100 ºC	[29] [49]	a) Strong dependency of permeability on chemical structure polyamides b) Linear relationships in Arrhenius permeability vs. temperature
Poly(2,6 dimethyl-1,4-phenyleneoxide) tetramethyl polycarbonate	15-45 ºC	[50]	Smaller temperature dependency of permeability
Polycarbonate, Tetramethyl carbonate, Tetramethylhexaflouropolycarbonate	35-200 ºC	[24]	Observation of Arrhenius behaviour i.e. increase in permeability with temperature
6FDA-DAF 6FDA-IPDA	35-55 ºC	[49]	Temperature dependency of permeability is smaller
Teflon AF 2400	25-60 ºC	[51]	Negative permeation activation energies
Poly(4-methylpentene)	20-45 ºC	[52]	Slope discontinuity near Tg (40ºC), 34 ºC
6FPPy-6FPBA 6FPPy-BPA 6FPT-6FPBA 6FPT-BPA	120-155ºC	[46]	Higher permeation in 6FPPy than 6FTP but similar selectivities

Haraya and Hwang [50] in 1992, studied the temperature dependency of gas transport properties of polycarbonate (tetramethyl bisphenol-A) (TMPC) and poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) membranes in the temperature range of 15-45ºC. In this study, it was observed that, the temperature dependency of the permeabilities for these three polymers was relatively smaller than for other typical glassy polymers and it was concluded that this relatively small activation energy for permeation in PPO and TMPC was due to primarily the significantly lower activation energy for diffusion compared again with the other polymers.

Pinnau and Toy [51] in 1996, measured the permeability coefficients of Teflon AF 2400, which is an amorphous, glassy perfluorinated copolymer, at a temperature range of 25 to 60 ºC to determine the temperature dependency of membrane gas permeabilities. In this study it was observed that, Teflon AF 2400 shows only a very weak dependence of gas permeability on temperature. The activation energies of permeation for gases were slightly negative, that was permeability decreased with increased temperatures. Negative permeation energies of gases were routinely observed for microporous solids in which the pore dimensions are relatively large in comparison with the diffusing gas molecules. So, Teflon AF 2400 may comprise a network of interconnected gaps with dimensions large compared to the diffusing gas molecules.

Kaniuzawa et al [52] in 1994, examined the processes of gas sorption and permeation in poly(4-methylpentane) (PMP), at temperatures above and below the glass transition point (T_g). For both O_2 and N_2 gases, the Arrhenius plots can be approximated by two straight lines and at around T_g the slopes of the lines were different due to the structural changes in polymers from rubbery to glassy state at T_g.

The permeation activation energies of different gases and different polymeric films of which the temperature dependency of permeation activation energy are examined and are reported in Table 2.4.2. These polymeric films are mostly based on glassy polymers except for rubbery polycarbonate.

Table 2.4.2 Permeation activation energies of various polymers for different gases

Polymer	**E_p*(N_2)**	**E_p*(O_2)**	**E_p*(He)**	**E_p*(CH_4)**	**E_p*(CO_2)**	**Ref**
PTMSP	-1.22	-1.46	-0.096	-1.51	-2.32	[51]
Teflon AF 2400	-0096	-0.6	0.38	0.31	-1.60	[51]
Polycarbonate	6.0	4.7	4.2	6.2	3.0	[24,51]
Rubbery PC	10.3	-	4.6	12.8	7.9	[24]
6FDA-DAF	3.49	2.3	2.0	4.73	0.9	[49]
6FDA-IPDA	4.66	3.05	2.7	5.84	1.2	[49]
TMPC	4.0	2.8	3.0	4.5	1.6	[24]
TMPC	3.51	2.48	-	-	-	[50]
TMHFPC	3.0	2.1	2.3	3.7	0.4	[24]
PPO	2.44	1.63	2.53	-	-	[50]
6FPPy-6FPBA	8.97	7.41	-	10.67	1.49	[46]
6FPPy-BPA	11.98	8.73	-	10.66	2.54	[46]
6FPT-6FPBA	13.76	8.86	-	12.47	3.11	[46]
6FPT-BPA	10.09	10.06	-	12.29	4.03	[46]

*All E_p values are given in kcal/mol

As this table demonstrates, the permeation activation energy for rubbery polymeric membrane, rubbery polycarbonate, is higher than for glassy polymeric membranes. Some negative activation energies are also reported due to the ultrahigh free volume of these polymers resembling microporous solid structure. Comparison of E_p, and permeability values of two TMPC reported ([24] and [50]) shows that the membrane preparation technique also affected these values. In [49], annealing of membranes were done above T_g of TMPC but, in [24], annealing temperature of TMPC membranes was only 25 ºC which is below T_g of TMPC.

Z-K. Xu et al [46] studied four novel poly(arylene ether)s as mentioned in the previous section. Comparing the gas separation properties between these membranes, 6FPPy membranes show higher gas permeability coefficients than the 6FPT membranes and show similar selectivities. These results are related to the gas diffusion in the membrane and are attributed to the polymer structure. The effect of temperature on the gas transport properties of these membranes between 30 and 75ºC and the corresponding activation energies for gas permeation, calculated from the Arrhenius equation, are listed in the Table 2.4.2.

2.4 Mixed Matrix Membranes

The physical structure of polymeric membranes can be classified under two distinct morphology: Homogeneous and heterogeneous. The simplest morphology is homogeneous polymeric membrane, which was the area of interest in the first period of membrane development. Homogeneous polymeric membrane morphology is composed of a nonporous dense single layer which is homogeneous in all directions. To yield higher selectivity and higher fluxes for technological applications, heterogeneous membranes were developed by applying novel morphologies. Asymmetric, composite and mixed matrix membranes are the major morphologies of heterogeneous membranes that have been developed to this date [15]. Asymmetric membranes are considered to consist of a dense homogeneous skin layer supported by porous backing of the same material. On the other hand, composite membranes are formed by deposition of highly permeable polymeric material on a porous membrane of a different kind with a thin and homogenous layer. The latest emerging morphology is mixed matrix membrane which consists of two interpenetrating matrices of different material formed by thorough blending.

Gürkan et al [53] focused on the separation of O_2 /N_2 and H_2 /N_2 gas pairs using a zeolite 13X-filled polysulfone membrane made by extrusion. They reported a substantial increase in the selectivities of the H_2 /N_2 gas pair over the pure polysulfone membranes.

Jia et al [54] investigated the permeations of He, CH_4, N_2, O_2, CO_2, by using a membrane composed of polydimethylsiloxane (PDMS), a rubbery polymer and silicalite-1, a hydrophobic zeolite. They observed that increasing silicalite content in the composite membranes, the permeabilities of He, H_2, O_2 and CO_2 also increased, while the permeabilities of N_2 and CH_4 decreased. The selectivity of H_2/N_2 was increased from 2.3 to 7.3 by increasing the silicalite content from 0 to 70 wt%. They concluded that silicalite played the role of a molecular sieve in the membrane by facilitating the permeation of smaller molecules, but hindering the permeation of larger ones.

Duval and coworkers [55] studied the effect of the introduction of specific adsorbents on the gas separation of polymeric membranes. They observed that zeolites such as silicalite-1, 13X and KY improve to a large extent the separation properties of poorly selective rubbery polymers for a mixture of CO_2 /CH_4. However, zeolite 5A leads to a decrease in permeability and an unchanged selectivity due to the impermeable character of these particles. Carbon molecular sieves also do not improve the separation performances resulting from the dead-end porous structure which is inherent to their manufacturing process.

Koros et al [6] investigated the fundamental gas transport properties of thin films of six high performance polymers in the presence of silicon dioxide particles. The presence of silica improves the properties such as an increase in the permeability of O_2 resulted in an increase in the selectivity of O_2/N_2. They suggested that the higher rigidity of the local matrix in more tightly packed region result from the adsorption of polymer to the surface and this attraction requires a larger amount of thermal energy to open a transient gap for diffusion of a penetrant in critical constricted regions in the polymer/silica composites. This is different from the structures of carbon molecular sieves (CMS) and zeolites which derive their special properties from an entropic selectivity feature, on the other hand, the silica modified polymer conforms to the traditional notions of selective transport in polymer, since energetic selectivity is the dominant feature.

Drioli et al [56] studied the influence of the filler on overall membrane permeability resulting in an upper and a lower limit of the permeability given the filler content and the permeability of the continuous phase theoretically. They related the permeability of a dispersion to the permeabilities of the continuous and dispersed phase, and the volume fraction of the dispersed phase by the equivalence between the dielectrics and permeation in dense membranes.

Tanioka et al [57] investigated the effects of carbon filler on the sorption and diffusion of CO_2 in natural rubber and in styrene-butadiene rubber. They observed that the permeability coefficient increased very slightly at low carbon content and then decreased owing to geometric effects of polymer chain immobilization in the interfacial regions. Sorption isotherms obey to Henry's law in unfilled rubber and to Langmuir's law in carbon black, so the isotherms in filled rubber exhibit a combination of the two sorption modes.

Suer et al [58] focused on the type of zeolites and their amounts introduced into Poly(ethersulfone) (PES) polymer and the effect of membrane preparation procedure on the transport properties of membranes. The permeability measurements of single gases N_2, O_2, Ar, CO_2 and H_2 were carried out with a variety of membranes prepared at different zeolite loading. Significant changes in the membrane morphologies of PES-13X and PES-4A matrices were observed implying the importance of zeolite type. Their SEM studies showed that the addition of zeolite particles induced a microporous cavity and channeling system demonstrating the polymer-zeolite interactions and partial incompatibility. They concluded that the types of membrane preparation procedure and types of zeolite strongly affect the transport properties of membranes. The permeability coefficients of all gases have decreased till 8 wt% loading for zeolite 13X and 25 wt% loading for zeolite 4A, but at higher zeolite loading, a recovery in permeabilities have started favoring the permselectivities. Therefore, in both matrices the gas transport properties were enhanced at high zeolite loading for certain commercially important gas pairs due to faster permeation of H_2 and CO_2 through the membrane matrix. They concluded that increase in the selectivities with the increasing filler content could not be solely due to molecular sieving mechanism. The shape selective properties of zeolites, polarity of gases and micro structure of membranes might play roles in increasing permselectivities.

Battal et al [59] measured the permeabilities and the selectivities of CO_2/CH_4, CO_2/Ar and H_2/CH_4 binaries as a function of gas composition through a dense homogeneous PES membrane and a PES-4A mixed matrix membrane.

Observed selectivity independence with respect to gas composition for a dense homogeneous PES membrane indicates that ternary interactions and factors like plasticization and gas fugacity do not affect the gas permeation mechanism appreciably for this type of membrane. However, the selectivities demonstrated a strong concentration dependency through a PES-4A mixed matrix membrane. For CO_2/CH_4 and CO_2/Ar systems, when the CO_2 concentration in the feed increased, the selectivities decreased linearly. In the case of H_2/CH_4 binary, unlike the cases with CO_2 binaries, a higher H_2 concentration in the feed caused higher selectivity values. The trend was also linear with H_2 concentration in the feed. This indicates that for mixed membranes, the existence of a third component causes the gas molecules to interact with the heterogeneous membrane matrix, affecting selectivities. They concluded that the selectivity dependency indicates the importance of gas-membrane matrix and gas-gas-membrane matrix.

Tsujita [60] investigated the effects of additives on polymeric membranes. He concluded that the polymer-filler system often raises its glass transition temperatures, indicative of restricted segmental motion of the polymer itself because of strong polymer-filler interaction and therefore, the permeability and diffusivity coefficients decrease with filler content. In the case of weak polymer-filler interaction the filler may form a void in the interface between the polymer and filler. Then the permeability coefficients increases considerably, indicating hydrodynamic permeation through the void or pore in the membrane matrix. These findings point to the need for the investigation of different polymer-filler combinations in order to create membranes with widely differing permeabilities and selectivities.

Tantekin-Ersolmaz et al [61] studied the addition of HZSM-5, NaZSM-5, 4A and 5A into the PDMS matrix. Different Si/Al ratios and different activation temperatures were tested and no improvements with respect to the n-pentane / i-pentane ideal selectivity of the original polymeric membrane were observed. They concluded that differences in interaction between the two chemically similar penetrants with the interphase region connecting the bulk polymer and dispersed zeolite phases resulted in the higher permeation rate of iso-pentane at higher zeolite loadings while n-pentane permeability was decreased.

Yong and coworkers [62] examined the effect of introduction of 2,4,6-triaminopyrimidine (TAP) into the polyimide membrane filled with zeolites. TAP enhanced the contact of zeolite particles with polyimide chains presumably by forming hydrogen bonding between them. It was observed that the amount of TAP to eliminate the interfacial void could be related with the number of hydroxyl groups of zeolites. The void-free PI/zeolite 13X/TAP membrane showed higher gas permeability with little expense of selectivity compared to the PI/TAP membrane while the PI/ zeolite 4A/ TAP membrane showed the lower permeability but higher permselectivity; the difference between both membranes were the pore size of the zeolite.

All above studies indicate that various zeolites, silica and carbon fillers were introduced to the matrix and due to incompatibility problems occuring between the matrix polymer and the fillers, striking improvements were not observed with these type of membranes.

Therefore, the effect of insoluble polymeric fillers, which is a new approach to the mixed matrix membranes, was decided to be performed. In recent studies of our group, Gülşen et al [63]and Hacarlıoğlu et al [65] researched the effect of conductive polymer filler on the permeability and selectivity properties. As the polymer matrix, polycarbonate (PC) was preferred due to its wide usage as membrane matrix in industry. As a conductive polymer, polypyrrole (PPy) was prepared with in-situ polymerization technique [63], electrochemical synthesis technique and chemical synthesis technique [64-65]. They experienced that even a small change in the synthesis procedure of supporting electrolyte, such as type or concentration of conducting polymer, strongly effects the morphology of the composite structure and permeability. They also recorded that decrease in PC content as increase PPy ratio deformed membranes. In this unique study through literature, some of the ratios of “conducting polymer / insulating polymer” promising and hopeful results were obtained.

With this study, we tried to develop a new kind of the mixed matrix membrane with the same knowledge of conducting polymer synthesis and membrane preparation procedure by changing polymer matrix.

2.5 Conductive Polymers

Polymers with conjugated Π-electron backbones which display unusual electronic properties such as low energy optical transitions, low ionization potentials and high electron affinities are called conducting polymers. Charge transfer agents affect this oxidation or reduction and in doing so convert an insulating polymer into a conducting polymer with a near metallic conductivity in many cases [66].

In their undoped state conjugated organic polymers are best described as electrical insulators. The conductivity, σ, is proportional to the product of the free carrier concentration, η, and the carrier mobility, μ,

$$\sigma = e \ \eta \ \mu \qquad (2.5.1)$$

where e is the unit electronic charge. For intrinsic conductivity, the carrier concentration decreases exponentially with increasing band gap. Since conjugated polymers have relatively large band gaps, the concentration of the free carriers is very low even though their backbone structures are well suited to conduction, this low carrier concentration results in negligible conductivity [66].

The doping of conjugated polymers generates high conductivities primarily by increasing the carrier concentration. This is accomplished by oxidation or reduction with electron acceptors or donors, respectively. For example, the polymer is oxidized by removal of an electron, thereby producing a radical cation (or hole) on the chain. If the hole can overcome the coulombic binding energy to the acceptor anion with thermal energy or, at high dopant concentrations, it moves through the polymer and contributes to the conductivity.

2.5.1 Electrically Conductive Gas Separation Membranes

There are considerable researches performed on the subject of developing electrically conductive gas separation membranes.

Kuwabata and Martin [67] worked on free standing polyaniline membranes and observed that both rate and selectivity in gas transport depend on the doping level. Permeability coefficients far all gases studied was observed to decrease with increasing doping level and selectivities to increase with doping level. Both freestanding polyaniline and thin film composite membranes showed identical rates and selectivities of gas transport. The highest O_2/N_2 and CO_2/CH_4 selectivity coefficients obtained were 15 and 55 respectively.

Anderson et al [12] also studied freestanding films of polyaniline and found remarkable selectivities for important gas pairs such as H2/N_2, O_2/CH_4. They observed that the doping/undoping of polyaniline leads to one of the most selective membranes known. The selectivity values of 3590 for H_2/N_2, 30 for O_2/N_2 and 336 for CO_2/CH_4 surpass the highest previously reported values of 313, 16 and 60 respectively for the non-conjugated polymers. They also showed [69] how selective control of gas permeability is facilitated by the doping, undoping and redoping process of emeraldine films. They observed a large increase in permeability to all gases following the doping and undoping treatment cycle. Also, controlled redoping of the undoped films result in large separation factors for industrially important gas pairs. They concluded that this behavior was consistent with the model based on dopant occupation of free volume of the “pin-hole free” film.

Kuwabata and Martin [67] and Anderson et al [12] both worked with polyaniline membranes, however, the gas-transport selectivity data presented by these two groups were considerably different. Anderson et al reported gas selectivities of O_2/N_2=30 and CO_2/CH_4=336, whereas, Kuwabata and Martin reported 15 and 55 respectively for the same gas pairs. Kuwabata and Martin [67] thought that this difference might be attributed to the fact that polyaniline was present as thin supported film rather than a thick freestanding film in their method.

They therefore, also investigated the transport properties of freestanding polyaniline films. These membranes showed transport properties identical to those of their supported thin films; i.e., again, they were not able to reproduce the exceptional transport data obtained by Anderson et al [12].

Escoubes, Rebatter and coworkers [68] performed a similar study with polyaniline membranes. Their investigation was doping the membrane in a strongly acidic medium, undoping it in a basic medium and redoping in a slightly acidic medium. From the variations in permeability coefficients with the doping treatment, they divided the gases in two subgroups according to the diameters of gas molecules, compromising H_2, O_2 and CO_2 (<3.5 ˚A) on one hand and N_2 and CH_4 (>3.5 ˚A) on the other. After the doping-undoping-redoping process they observed that gas fluxes were increased by 15% for the smaller gases and were decreased by 45% for the larger ones. Within subgroup, the variations in the permeability values with the doping, undoping and redoping treatment are strictly similar. Anderson et al have also evidenced that the doping-undoping-redoping process enhances the permeabilities of smaller gases and decreases the permeabilities of larger gases [69].

Rebatter et al [70] used emeraldine base, doped with HCl (4M), dedoped with NH_4OH (1M) and redoped with HCl (10^{-2}M). They observed linear sorption for N_2 which corresponds to an ordinary dissolution in Henry's law state. Non-linear isotherms of O_2, CH_4, CO_2, could be described by dual-mode sorption mechanism proposed for glassy polymers which consists of the combination of a Henry's type dissolution with Langmuir sorption in relaxed gaps between macromolecular chains. The doping-dedoping-redoping cycle also favors the creation of microcavities which able to trap molecules following a Langmuir isotherm. The specific interactions between PANi and O_2, CH_4, CO_2 were discussed and Langmuir sorption is attributed to a paramagnetic interaction for O_2, the partial molar volume theory developed by Kirchheim for CH_4, acid-base interaction for CO_2. The gas permeation experiments also confirmed the dual mechanism for O_2, CO_2 and Henry's dissolution observed with N_2. They also indicated that high selectivity values observed by Anderson [12] for the O_2/N_2 gas pair cannot arise from a difference in solubility factors.

Wang and Mattes [71] worked on polyaniline films at varying temperatures. They observed the permeability of gases is temperature dependent and increases with increasing temperature; however, the permselectivity of gas pairs He/N_2, O_2/N_2, CO_2/CH_4 decreases with increasing temperature. The activation energy for permeability was determined from the isobaric measurements which shows that the order for activation energy is $He \sim H_2 \sim CO_2 > O_2 > N_2 > CH_4$.

Mattes et al [69] pointed out that gas permeability through polyaniline membranes can be controlled in a number of different ways. They declared that the acid choice, which is used for cycling the film, and the annealing during membrane formation step are very important control parameters. They also made polyaniline-polyimide blends that form selective barriers to the penetration of gases. They demonstrated that other conducting polymer systems such as poly(dimethoxyparaphenylenevinyline) (DMPPV) behave similarly to polyaniline films.

Martin et al [72] studied conductive polymers as selective layers for membrane based gas separation. For this purpose they used interfacial polymerization to synthesize thin films of polypyrrole, poly(N-methylpyrrole), polyaniline onto the surfaces of microporous support membranes. They found O_2/N_2 selectivities of 7.9 and 6.2 and CO_2/CH_4 selectivities 16.2 and 31.9 for doped poly(N-methylpyrrole) and undoped poly(N-methylpyrrole) respectively concluding that the introduction of ionic groups into a polymer lowers the available void volume thus a decrease in permeabilities of doped poly(N-methylpyrrole) was observed.

Kamada et al [73] synthesized polypyrrole and poly(N-methylpyrrole) in the micropores of Vycor glass to prepare microporous composite membranes by means of chemical oxidative polymerization. They observed high selective gas permeation of O_2 to give a separation factor greater than 3 for N_2. The mechanism of gas flow through the membrane was considered to be surface flow based on various experimental results, such as isothermal gas sorption, pressure dependence of GPR and membrane structure were obtained by BET method.

Martin and Parthasarathy [13] experienced very unusual gas transport selectivities in the partially oxidized form of polypyrrole. They prepared membranes by slowing down the rate of polymerization reaction of polypyrrole with dense morphology. They showed that a partially oxidized form of this material displays extraordinary gas-transport properties. They synthesized PPy as ultra thin films across both surfaces of polycarbonate support membrane and obtained the O_2/N_2 selectivity coefficient of 18. A rather interesting result they came across was that the selectivity ratio was increasing as the partial pressure of O_2 in the feed gas stream decreases and reaching to 92 when the partial pressure was dropped to 0.1%.

Mussellman et al [74] casted freestanding poly(3-dodecylthiophene) membranes. The permeability values measured for this membrane were 9.4, 20.2, 88.2 Barrers for N_2, O_2 and CO_2 respectively. Chemically induced oxidation with $SbCl_5$ resulted in a decrease in permeability and a corresponding increase in permselectivity while the reduction of the oxidized membrane with hydrazine partially reserved these trends.

Mussellman [75] and his coworkers reported the gas transport properties of surface-treated poly(3-(acetoxyethyl)thiophene) membranes. Both acidic and basic hydrolysis of the surface of this ester yielded poly(3-(2-hydroxyethyl)thiophene), a highly permselective conducting polymer. The calculated values were drastically increased: The selectivity values of the poly(3-(acetoxyethyl)thiophene) were 5.1 for O_2/N_2 and 18.5 for CO_2/CH_4 whereas values of base-treated poly(3-(2-hydroxyethyl)thiophene) were 12.9, 20.0 and values of acid-treated poly(3-(2-hydroxyethyl)thiophene) were 11.7, 45.0 for the same gas pairs respectively.

As mentioned previously, in one of the studies of our group [63], membrane performance of mixed matrix composites of polypyrrole (PPy) with poly(bisphenol-A-carbonate) (PC) were prepared by a combined in-situ solution polymerization. The effects of the PC content, hydrophilicity or hydrophobicity of casting surface, annealing, solvent evaporation temperature, evaporation time, and supporting electrolyte type and concentration on the membrane performance were investigated and observed that the electrolyte type and its concentration determine the morphology of the membrane and the size and shape of electrolyte affect membrane performance. During preparation of these membranes PPy could be introduced in low amounts. Thus, this brought the idea of using conducting polymers as powder fillers for preparation of mixed matrix membranes.

As a next study, the polymer couple PPy and PC was used to develop a new version of previous study [64]. The electrochemically synthesized PPy films were converted to powder so that the conducting polymer could easily be introduced in the dissolved insulating polymer. The resulting mixed matrix membranes were more permeable without an appreciable loss in selectivity compared to pure PC membranes.

To go further on the idea of using conducting polymers as filler, recently a different technique was developed as a future work in our group. The PPy filler powder was synthesized chemically instead of electrochemically synthesis [65] and introduced into the dissolved insulating polymer PC in different ratios. Especially when considering the selectivities of industrially important gas pairs, like O_2/N_2, CO_2/CH_4, the success of chemically synthesized PPy filler containing PC membranes was clearly seen. Contrary to the electrochemically synthesized PPy-PC membranes, chemically synthesized PPy-PC membranes were a little less permeable but much more selective. The importance of filler preparation technique was examined once more. With this study, the optimum filler preparation of conducting polymer was developed. To pass the limits for performance of conducting polymer-insulating polymer mixed matrix membrane system, there was a need to a new kind of insulating polymer. Thus, this brought the idea of using a polymer (like PEK's) with higher temperature resistance and better mechanical properties compared to poly(bisphenol-A-carbonate).

CHAPTER 3

EXPERIMENTAL

3.1 Materials

The insulating polymer, hexafluorobisphenol A based poly(arylene ether ketone) (PAEK) was synthesized in Turkish Scientific and Technical Research Center, Gebze. [40]

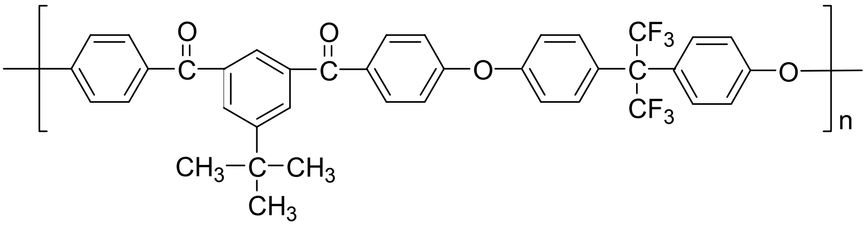


Figure 3.2.1 Hexafluorobisphenol A Based Poly(arylene ether ketone), (PAEK)

Pyrrole was purchased from Aldrich Chemicals and vacuum distilled prior to use.

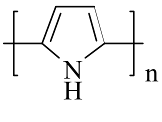


Figure 3.2.2 Polypyrrole, (PPy)

Chloroform was purchased from Aldrich Chemicals. Iron chloride was supplied by Riedel De Haen AG. Paratoluene sulfonicacid monohydrate (98%), PTSA, was obtained also from Aldrich Chemicals. All the chemicals are analytical grade and used without further purification. The gases N_2, CH_4, Ar, H_2, CO_2 and O_2 were supplied by local companies.

3.2 Membrane Characterization

Membranes were analyzed thermally to observe the amount of the residual solvents by 951 Dupont Thermal Gravimetry Analyzer (TGA). The heating rate was 10°C/min in N_2 Atmosphere.

For the characterization of membrane morphology, electron micrographs of membranes with different conductive filler concentrations were obtained. For this purpose, Scanning Electron Microscopy on JEOL JSM-6400 was used.

3.3 Conductive Polymeric Filler Preparation Procedure

Chemically synthesized conductive polypyrrole granules were reduced to powder form in size, and then added to the insulating PAEK polymer matrix to obtain a conductive mixed matrix membrane.

Polypyrrole was chemically synthesized in water by mixing a solution of pyrrole with an oxidizing solution of $FeCl_3$. Based on literature precedure [76], the synthesis was allowed to proceed at 5-7 °C and the molar ratio of Fe^{+3} / Pyrrole was taken as 2.3, and the molar ratio of dopant (PTSA) / Pyrrole was taken as 0.3. In our experiments, the pyrrole concentration was fixed to 0.1 M as the determining ratio for the other concentrations; accordingly other concentrations were calculated to be 0.23M for Fe^{+3} and 0.03M for PTSA. Therefore, for obtaining 500 ml final solution, first 31.05 g $FeCl_3.6H_2O$ (270 g/mole) was dissolved in distilled water, then 2.85 g PTSA (190 g/mole) and 3.5 ml Pyrrole (0.967 g/ml , 67g/mole) were added respectively with a continuous magnetic stirring in an ice bath maintained at 5-7 °C. After 5 min., the solution was left for 6 hours without agitation. The polypyrrole precipitate was collected by filtration, and rinsed with distilled water. Afterwards, the washed polypyrrole precipitate was dried in the oven at 50 °C. These precipitates were crushed into powder form in liquid nitrogen and made ready to be used as the filler. The particle size range of PPy powders was between 0.5-3μm and conductivity of resulting material was recorded as 0.6 S/cm [65].

3.4 Membrane Preparation Methodologies

Dense homogeneous flat sheet poly(arylene ether ketone) (PAEK) membranes were prepared by solvent evaporation. The PAEK polymer was dissolved in chloroform in a constant composition of 5% (w/v) and drop casted by pouring into a petri dish. The solution in the petri dish was placed in the oven (50 °C) for 30 min. for evaporation and 24 hours for annealing at 50 °C. Dense flat sheet thickness is measured to be 40-60μm. This procedure is summarized in Figure 3.4.1a.

For mixed matrix membranes the preparation methodology is as follows: Poly(arylene ether ketone) was dissolved in chloroform (CH_3Cl) 5% (w/v), polypyrrole filler was then added to the solution in different compositions (10-20% w/w, dry basis) and final solution was mixed with magnetic stirrer to a homogeneous paste before casted in the petri dish. The final solution is placed in oven (50 °C), left for 30 min for solvent evaporation and 24 hours for annealing as in the case of pure PAEK membranes. This time the thickness was in the range of 130-180μm. Figure 3.4.1b describes this procedure in detail.

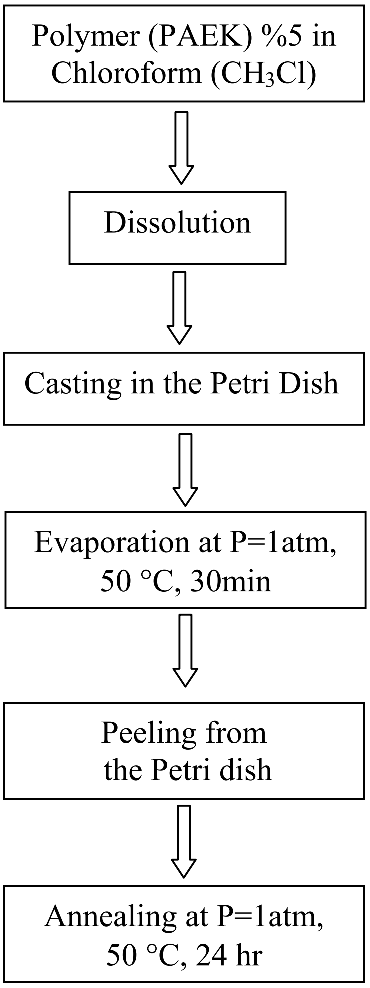


Figure 3.4.1a. Dense Pure polymer membrane procedure

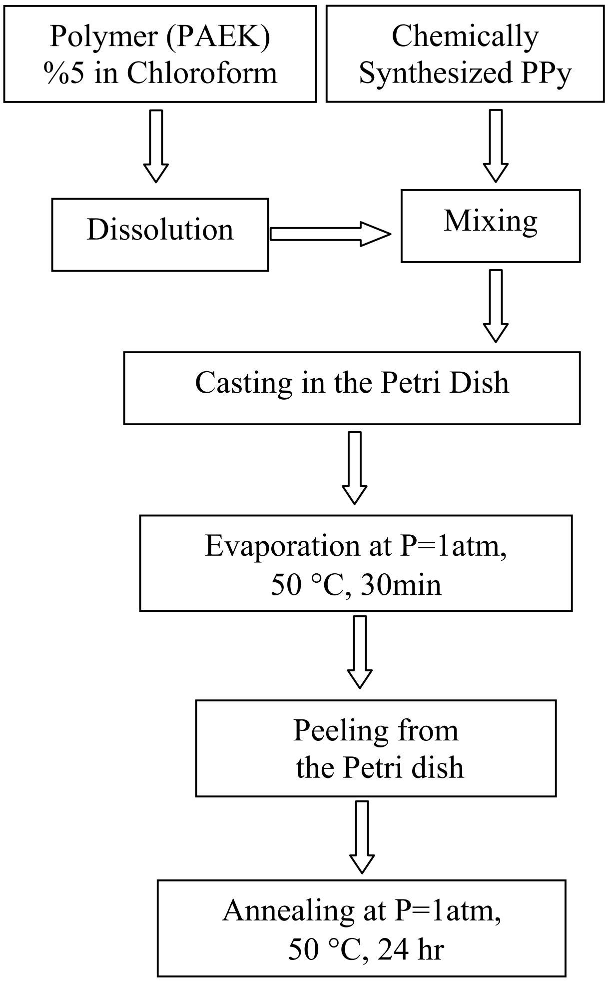


Figure 3.4.1b. PPy loaded Mixed Matrix membrane procedure

3.5 Gas Separation Measurements

3.5.1 Experimental Set-up and Measurements

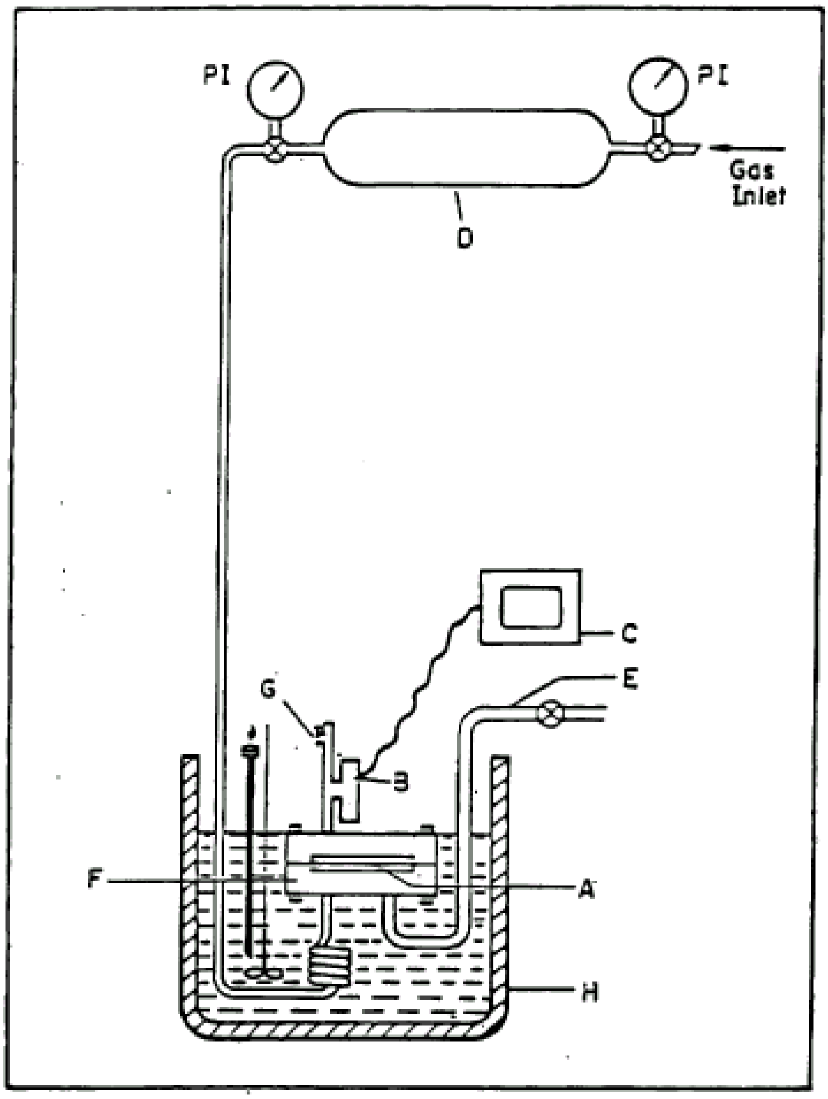
The experimental set-up used for determination of permeability of pure gases fulfills the requirements of ASTM D1435-82. The apparatus [64] which is shown in the Figure 3.5.1 consists of two thin cylindrical flange made of nickel-steel alloy 10 cm in diameter and 1.5 cm thick. Membrane is placed between these flanges with elastic rubber gaskets to prevent gas leakage and supported by filter papers in the same diameter of membrane. The flanges are clamped in six equally spaced different points placed on the edges of flanges. The apparatus including the flanges is immersed in the silicon oil bath, which lets the temperature to be controlled or constant.

For working at different operational temperatures, silicon oil bath is equipped with a heater and a cooler. Heater consists of a resistance and a thermocouple so when actual temperature reaches to the set point, heater switches off automatically. Cooling is maintained by circulating water within a narrow copper pipe positioned deep in the silicon oil. To obtain a constant temperature at every point in the silicon bath homogenously, a stirrer runs continuously during the whole experiment.

On the penetrant side, the lower flange has a high pressure line providing the connection to a the gas chamber where pure gases are collected. Also a high pressure purge line with a needle valve is connected the lower flange. On the permeate side, the upper flange has just a low pressure line with a needle purge valve before the pressure transducer.

Pressure transducer transmits the electrical voltage to an acquisition board and pressure increase on the permeate side versus time data were recorded by a computer. The data acquisition board and related software are specially designed and calibrated for the system [64].

The experimental measurements were performed by using constant volume-variable pressure technique. The penetrant gas taken from the gas cylinder was allowed to the gas chamber at around 40 psig and admitted to the high-pressure (lower) side of apparatus. The high pressure side of the membrane was first swept by the penetrant gas while the low pressure (upper) side valve and high pressure side was opened. The permeation was terminated by closing the low-pressure side valve while the high-pressure side was at around 40 psig and low-pressure side was at atmospheric pressure. The permeating gas flowing into the pressure transducer against atmospheric pressure causes the pressure increase in the pressure transducer and these values were recorded as a function of time. Before each measurement, both high and low pressure purge valves were opened and membrane was degasified by applying vacuum (0.1 atm) for about 30 minutes.



A : **Membrane**
B : **Pressure Transducer**
C : **Digital Meter**
D : **Gas Chamber**
E : **High Pressure Purge**
F : **Permeability Cell**
G : **Vacuum Port**
H : **Constant Temperature Bath**

Figure 3.5.1 The Permeability Apparatus

3.5.2 Treatment of Experimental Data

Data recorded by the computer software, which is previously explained, was treated by Windows Excel program for calculating the slope of the pressure difference vs. time graph by means of linear regression. It is shown in Figure 3.5.2.

The molar flow-rate of the permeate gas can be expressed as;

$$dn / dt = (dP / dt) .(V_d/RT) \tag{3.5.2.1}$$

where dP / dt is the steady state pressure difference by using ideal gas law. V_d is the dead volume that the permeate gas occupies in the low pressure side and T is the absolute temperature. For this apparatus dead volume was calculated to be 6 cm^3 in a previous study [77].

The volumetric flow rate of permeate stream, V, was evaluated by;.

$$V=(dn/dt) M (1/\rho) \tag{3.5.2.2}$$

$$\rho=(PM) / (RT) \tag{3.5.2.3}$$

where ρ is the density of the permeate stream, P is the permeate pressure, M is the molecular weight of the penetrant gas.

The volumetric flux of the permeate stream is expressed as;

$$J= V / A \tag{3.5.2.4}$$

$$A= \pi d^2 /4 \tag{3.5.2.5}$$

where A is the effective membrane area and d is the diameter of tested membrane.

The diffusion through polymeric films at steady state is described by Fick's law;

$$J= - D\, dC / dX \tag{3.5.2.6}$$

And Henry's law is generally assumed to apply in gas permeation;

$$C= H P \tag{3.5.2.7}$$

Therefore, the combination of them indicates the mean permeability coefficient of any component with the following equation.

$$P= ([V/ (\pi d^2 /4) \delta] / [P_h-P_l]) \tag{3.5.2.8}$$

where δ is the thickness of the membrane, P_h and P_l are the pressures of high and low pressure side respectively.

A simple computer program written in Windows Excel is used for calculations of permeability measurements including the regression of pressure versus time graph. Final permeabilities of each gas through specified membrane were evaluated by taking the arithmetic mean of these runs. [64]

The ideal separation factor can be calculated from the ratio of the permeability coefficients of each gas, which can be expressed as;

$$\alpha_{ij} = P_i / P_j \qquad (3.5.2.9)$$

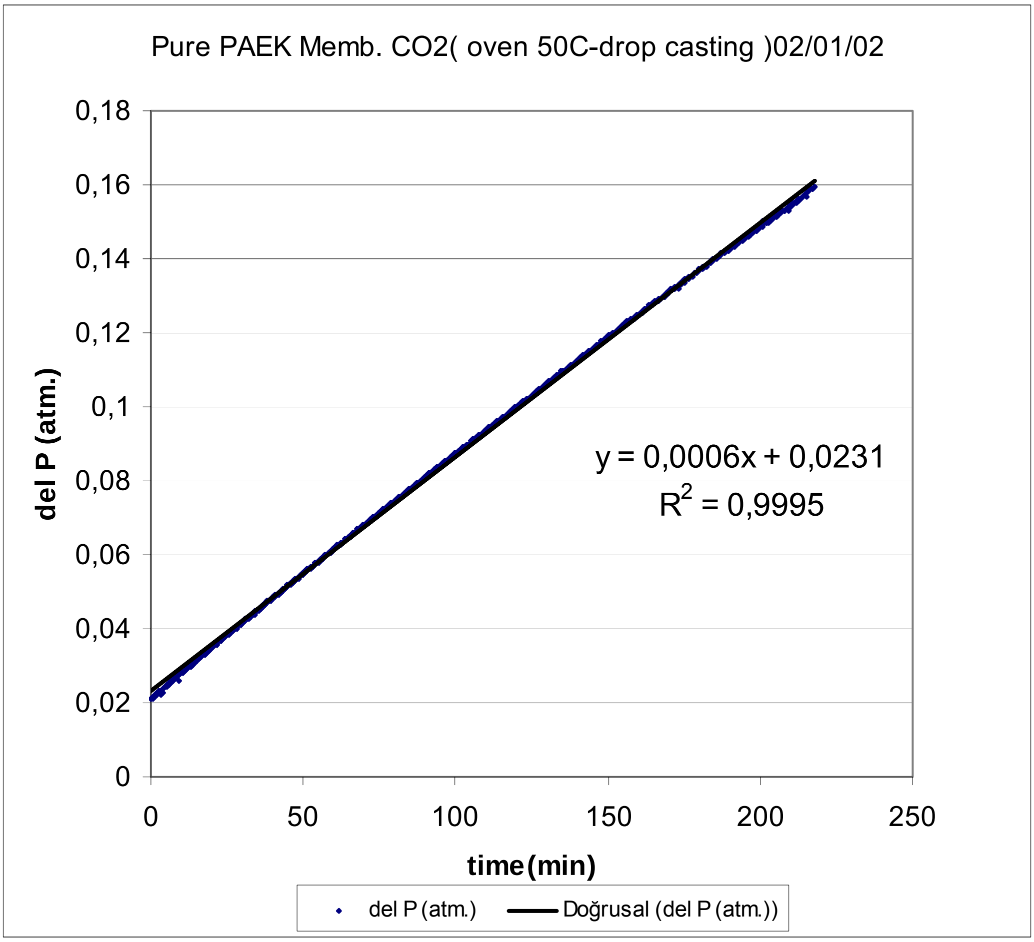


Figure 3.5.2 Pressure Difference as a Function of Time for CO_2 Through PAEK membrane

CHAPTER 4

RESULTS AND DISCUSSION

In previous studies various preparation parameters like evaporation and annealing temperature of membranes were examined [48, 64]; different conductive polymer synthesis routes were tried with mainly polycarbonate polymer matrix [59, 63, 65]. As a continuation, in this study, a different polymer matrix was chosen due to its good mechanical properties and higher T_g when comparing with polycarbonate.

In this study, hexafluorobisphenol A based poly(arylene ether ketone) (PAEK) and its polypyrrole composite membranes were studied. Due to its high mechanical properties, to test this new polymer, PAEK, as a membrane matrix was the first target. For this purpose, dense homogenous PAEK membranes were characterized by studying different operational temperatures (ranging from 25 ˚C to 85 ˚C); temperature effect on the permeability behavior this material for the gases N_2, CH_4, Ar, H_2, O_2 and CO_2 was observed. Other target of this study was to investigate the effect of conductive polymer filler to the permeability and selectivity properties on this new polymer matrix. The chemically synthesized polypyrrole, which was used as conductive polymer filler (at loads of 10% and 20%), was applied to this study due to its promising properties in previous studies.

4.1 Reproducibility of Experiments

To test the validity of the methodology and to check the gas permeation apparatus and the membrane preparation procedures, a series of reproducibility experiments were carried out. The permeability of each gas through each cast of membrane was measured at least for 3 runs. For these successive runs the relative error for the permeability was calculated to be between 2-7% with dense homogeneous PAEK membranes at 25 °C. When considering the selectivities of these membranes, the relative error almost stayed constant between 3-7%.

Same relative error calculations for permeability and selectivity values were applied to the results of measurements done for investigating temperature effect. At three other different temperatures (50, 70 and 85 respectively), relative error increased very slightly to the range of 4-8% as expected. Considering the selectivity values, this error was dropped to 3-7%. However slight variation in permeability of nitrogen and methane, which have very close permeability values, caused a large relative error in selectivity reaching to 20%, since nitrogen permeability value is used as divisor for calculations of ideal selectivity.

The permeability of each gas through PAEK-PPy mixed matrix membranes measured at least two times and the observed relative error for the permeability was 5-10% and the error for the corresponding selectivities was 4-13%. To reproduce exactly the same type of PPy loaded PAEK membrane, previously used membrane materials were re-casted. In other words, each previously used membrane was the raw material of the next one. Therefore, when considering mixed matrix structure, almost slight relative errors was recorded in PAEK-PPy mixed matrix membranes. (Results of the reproducibility measurements are given in Appendix).

The deviations in permeability and selectivity values were acceptable [63,64] and showed that the single gas permeation system and the methodology were reliable and workable dense homogeneous PAEK membranes and PAEK-PPy mixed matrix membranes could be reproducibly prepared.

4.2 Studies with Dense Homogeneous PAEK Membranes

Thermal characteristics of a polymer used for membrane preparation are important, knowing that these can be a function of physical properties of the polymer such as molecular weight, tacticity, degree of polymerization etc. As presented in Figure 4.2, thermal gravimetry analysis shows that 6FBisA PAEK is stable up to 539 ˚C [40] which points at good temperature resistance.

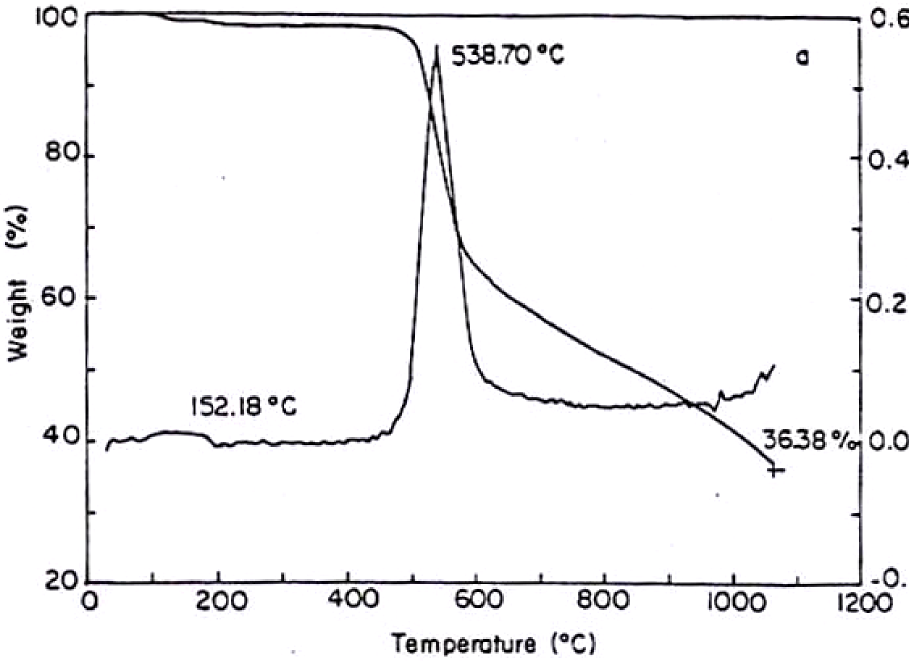


Figure 4.2 Thermal gravimetry analysis of PAEK (6FBisA)

Glass transition temperature value is also needed to be accentuated to test temperature resistance. On increasing the temperature, the physical and chemical properties of polymers change and they finally degrade. The extent of such change depends on the type of polymer with roughly speaking the glass transition temperature T_g being an important parameter for glassy amorphous polymers. T_g increases in existence of a rigid main chain consisting of aromatic and/or heterocyclic groups without any flexible (-C-C-) groups like in the PAEK (6FBisA). Also the large fluorine atoms in the $–C(CF_3)_2–$ group hinders molecular rotations within the backbone. The $–C(CF_3)_2–$ group interferes with other segments during conformational rearrangements, thus decreasing chain mobility such that the glass transition at a high temperature [42]. Reported T_g value of PAEK is 185 ˚C [40] which falls into a mid point of the values ranging from 150 ˚C to 250 ˚C [43-47] when comparing to the other poly(ether ketone)s in the literature.

When comparing PAEK with previously studied polymer polycarbonate, it can be reported that PAEK has higher thermal stability considering the total weight loss observed for PAEK (538 °C whereas 180 °C for PC).

At T_g point relaxed chains lets the solvent evaporates completely; even the trapped solvent liberates from the polymer matrix. Thus, one can get rid of any effect of solvent by reaching up to T_g. However, during the experiments, high evaporation or annealing temperature like 185 ˚C caused defects on the membrane film. Fast evaporation occurring with high temperature created bubbles on the surface which weakens the mechanical strength of membrane and demolishes the homogeneity. Therefore, lower evaporation temperature for long periods of time preferred. These previously optimized membrane casting processes [48,63,64] were applied to obtain the appropriate permeability behavior and flux.

Table 4.2 Permeability and selectivity data for dense homogenous flat sheet PAEK(6FBisA) membranes at 25 °C with ΔP= 40 psig (5% PAEK/CH_3Cl dried at 50°C for 30 minutes and annealed at 50°C for 24 hours)

Gas	Kinetic Diameter	PERMEABILITY (Barrer)	SELECTIVITY $\alpha(X/N_2)$
N_2	(3.64°A)	0.35	
CH_4	(3.86°A)	0.24	0.68
Ar	(3.4 °A)	1.15	3.28
H_2	(2.89°A)	15.8	45.1
CO_2	(3.3 °A)	7.31	20.8
O_2	(3.46°A)	3.20	9.14

In Table 4.2 permeability and selectivity values of PAEK membrane is tabulated. Permeability values of PAEK were found to be in the range of the reported values for various PEK's [41-47]. Literature values of permeability for CO_2 and H_2 ranges from 1.80 to 19.4 and 5.01 to 31.4 respectively. Permeability values were close to those obtained for PC [63-65]. However higher selectivities are obtained especially for O_2/N_2 pair. According to Robeson Plot [21] PAEK is only slightly below the upper bound showing superior performance than many other membrane polymers.

Rubbery polymers have weak binding forces between molecular segments, so that large molecules can move these segments to make themselves a channel to pass through. However, glassy polymers with high glass transition only let the small molecules pass through due to their stiff backbone. Glassy PAEK, having the bulky phenylene groups in its structure, certainly performed higher permeability for small gas molecules H_2 and CO_2, where as larger N_2 and CH_4 molecules were less permeable through PAEK.

On the other hand, O_2 showed high permeability than expected with respect to its kinetic diameter. As to the solution-diffusion mechanism theory of permeation, diffusion which is based on kinetic diameter of permeate molecules is not the only parameter. Even though all these gases have non-polar molecular structures, the affinity of O_2 for interaction with polymer molecule is much larger than other gases. One may speculate that since solubility is the main factor for O_2 permeation through PAEK, the permeability value was larger than expected.

Permselectivity values of PAEK showed fairly good especially for industrially important gas couples CO_2/CH_4, H_2/CH_4 and O_2/N_2 which are 30.45, 65.83 and 9.14 respectively.

4.2.1 Effect of Operating Temperature on Membrane Performance

The first parameter that was examined in this study was the effect of temperature to the permeability behavior of PAEK(6FBisA). Permeability measurements were done at four different temperatures 25˚C, 50˚C, 70˚C and 85˚C. Results of the permeability measurements were tabulated in Table 4.2.1.1.

Table 4.2.1.1 Permeability data of gases for Dense Homogenous PAEK membrane at increasing temperatures

	PERMEABILITY (Barrer)			
Gas	25 ˚C	50 ˚C	70 ˚C	85 ˚C
N_2	0.35	0.72	1.64	1.86
CH_4	0.24	0.63	0.97	1.62
Ar	1.15	1.97	3.12	3.75
H_2	15.8	37.6	57.6	73.0
CO_2	7.31	13.9	19.2	26.2
O_2	3.20	5.87	7.01	11.1

It can be also clearly observed through out the Figure 4.2.1.1 and Figure 4.2.1.2 that the permeability coefficients for all gases increase as the temperature increases linearly. Similar to other glassy polymers, increasing operating temperature gives rise to a strong increase in polymer segmental motions causing exponential increases in molecular diffusion rates. Generally a linear relationship between the logarithm of permeability coefficients and reciprocal of temperature is observed.

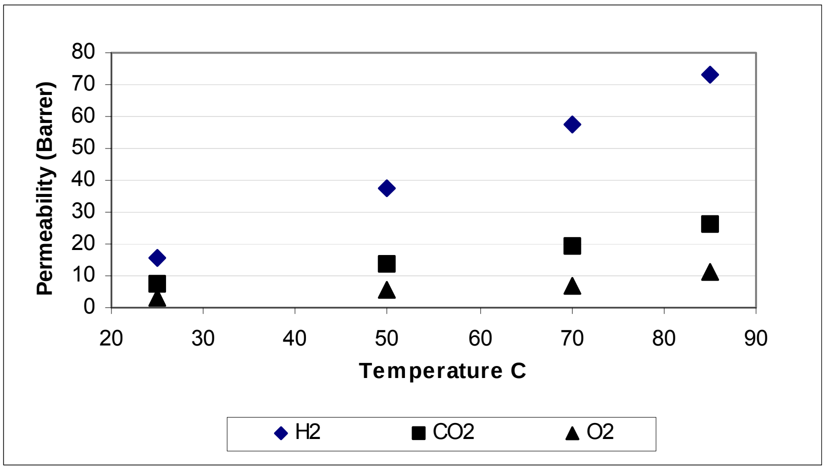


Figure 4.2.1.1 Permeability data of H_2, CO_2 and O_2 through PAEK (%5 w/v) membrane at increasing temperatures

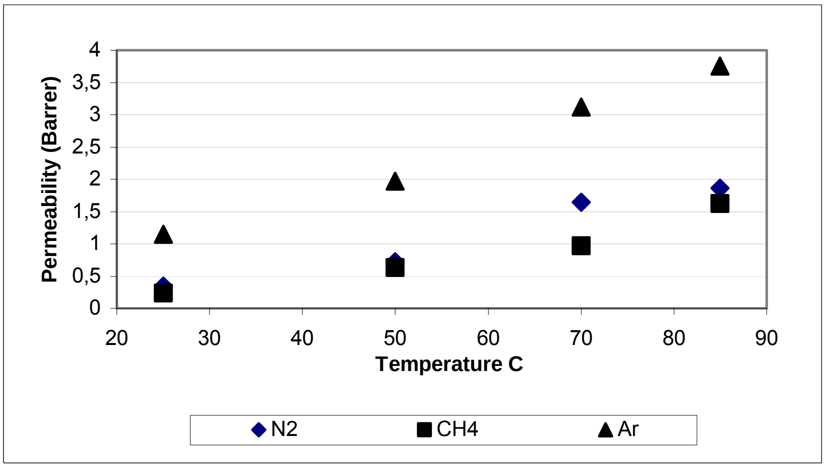


Figure 4.2.1.2 Permeability data of N_2, CH_4 and Ar through PAEK (%5 w/v) membrane at increasing temperatures

Increased segmental motions enhance the fractional free volume (FFV) thus, the diffusion of molecules increases. As expected smallest penetrant gas H_2 show a quite a high increase in permeability when temperature is increased, whereas stiff structure of PAEK with a limited FFV lets the largest gas molecule CH_4 permeate with a slight increase.

Table 4.2.1.2 Selectivity data of gases for Dense Homogenous PAEK membrane at increasing temperatures

	SELECTIVITYα (X/N_2)			
Gas	25 ˚C	50 ˚C	70 ˚C	85 ˚C
CH_4	0.68	1.14	1.7	1.15
Ar	3.2	2.7	1.9	2.0
H_2	45	52	35	39
CO_2	21	19	11	14
O_2	9.14	8.1	4.3	5.9

The selectivity values at different operational temperatures are tabulated above in Table 4.2.1.2. In most of the cases, higher temperatures tend to generate larger (less size discriminating) gaps in the polymer matrix which affects the selectivity in a negative way. At increasing temperatures, surprisingly, decreases in ideal selectivities of PAEK were very slight for most of the gases and almost constant for some other (Figure 4.2.1.3 and Figure 4.2.1.4)

G. Maier [44] reported that the functional groups does not affect the selectivity much but may have a large affect on permeability. Hexafluoroisopropyledene group is one of those and one may say that it is one of the reasons keeping the selectivity almost constant. Large and stiff arylene groups limits the segmental motions controlling the selectivity. Also large and stiff $(–C(CF_3)_2–)$ group obeys the main segmental behavior and does not cause a strong variation in selectivities at increasing temperatures.

Fortunately, with increasing temperature, no loss in selectivity was observed. Highest permeable gas H_2 showed an increase in selectivity when temperature rise was applied at first step. Ideal selectivity values of gases are calculated with permeability values of each gas divided by N_2 gas. Therefore, a slight increase in FFV with an increasing temperature may enhance H_2 more than N_2 permeability, so the selectivity ratio may increase for H_2 at first step of increasing temperature.

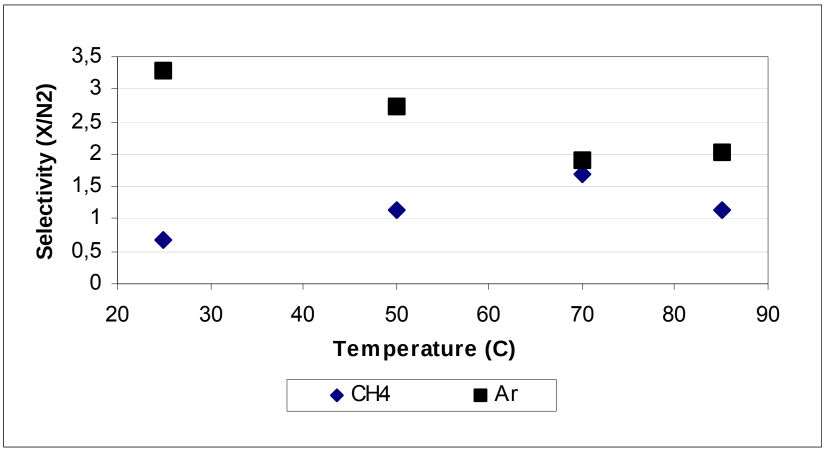


Figure 4.2.1.3 Selectivity data of CH_4 and Ar through PAEK (%5 w/v) membrane at increasing temperatures.

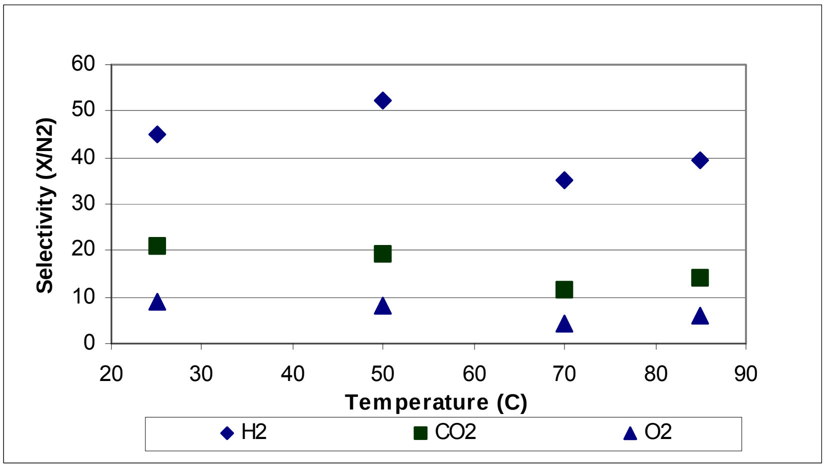


Figure 4.2.1.4 Selectivity data of H_2, CO_2 and O_2 through PAEK (%5 w/v) membrane at increasing temperatures.

4.2.2 Permeation Activation Energy of PAEK

The permeability of each penetrant in PAEK is an increasing function of temperature similar to other glassy polymers. According to increasing permeability by increasing temperature they were ordered as H_2>CO_2>O_2>Ar>N_2>CH_4. This order stays constant and the concord of permeability values are not disturbed even at high temperatures which reveals that Arrhenius law is valid for PAEK. This linear relation between the permeability coefficient and the reciprocal of temperature shows similarity with the reported permeation activation energy through other polymers and supported carbon molecular sieve membranes which follows almost the same trend with a variation of permeation gases. Figure 4.2.2 shows the Arrhenius plot of penetrant gases through PAEK membrane.

For most of the glassy polymers kinetic diameter of gases is the main factor which regulates the activation energy for permeation of penetrants which may be concluded on a large scale diffusion step of solution-diffusion mechanism constitutes permeation phenomenon. This causes evident activation energy differences depending on kinetic diameter of penetrants.

Table 4.2.2 Permeation activation energies of gases in PAEK Membrane

	N_2	CH_4	Ar	H_2	CO_2	O_2
E_p (kcal / mol)	5.94	6.05	4.02	4.99	4.11	3.78

However, the activation energies of penetrant gases in PAEK were calculated to be very close to each other. This may be because of the quite stiff structure of PAEK which limits the segmental motions and keeps the diffusion rates fixed and controls the permeability by sorption step of solution-diffusion mechanism.

In literature, there are also similar permeation activation energy values in the same order of magnitude which confirms with the stiff chemical structure of PEK's.

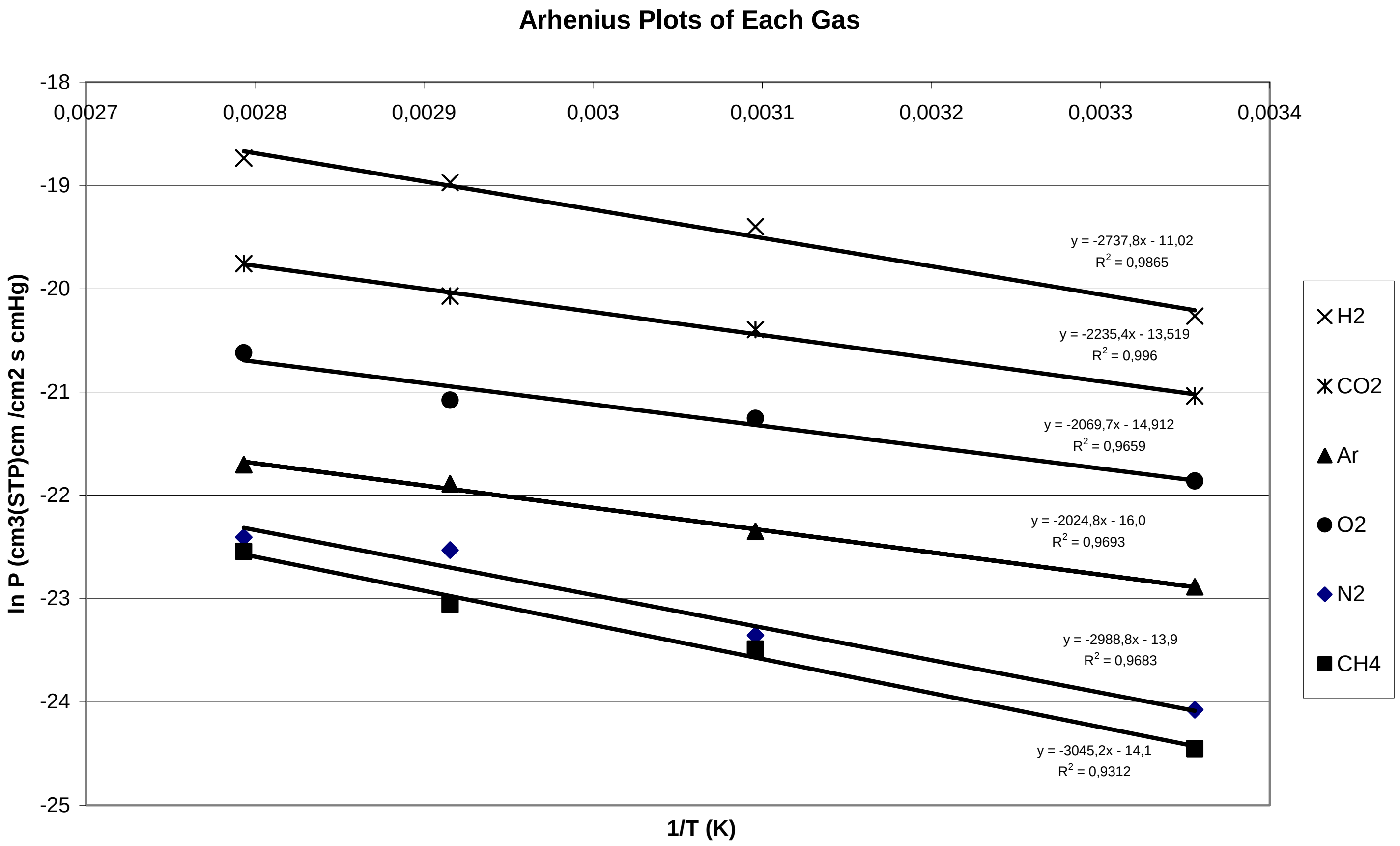


Figure 4.2.2 Arhenius Plots of Gases for PAEK Membrane

4.3 Studies with PAEK-PPy Mixed Matrix Membranes

4.3.1 Effect of Ratio of Filler Content to Matrix Polymer on Membrane Performances

The other important parameter investigated in this study was filler loading. Membranes were casted at different filler contents. The amount of matrix polymer PAEK kept constant and chemically synthesized PPy was added at different ratios to the matrix polymer dissolved in chloroform.

Using conducting polymer as a filler makes the conductivity measurements of mixed matrix membranes necessary. However, the four-probe conductivity measurements showed that this composite structure was a semi conducting material having less than 10^{-5} S/cm conductivity.

Chemically synthesized PPy was added to the PAEK-$CHCl_3$ solution at the ratios of 10%, 20% and 30%(w /w solid) and dried at 50 °C for 30 minutes and annealed at the same temperature for 24 hours just like that of dense homogeneous PAEK membranes. 30% loaded PAEK-PPy mixed matrix membrane was not workable. Even the surface was rigid and seemed to be homogeneous; the permeability values measured were quite high for all gases meaning that it contained too many pinholes and cannot function as a membrane.

Table 4.3.1 Permeability data at 25 °C for Dense Homogenous PAEK membrane and PAEK-PPy Mixed Matrix Membranes at 10% and 20% loads

	PERMEABILITY (Barrer)		
Gas	Pure PAEK	10% PPy Load	20% PPy Load
N_2	0.35	0.36	0.36
CH_4	0.24	0.69	0.99
Ar	1.15	1.08	1.25
H_2	15.8	14.9	15.4
CO_2	7.30	8.5	10.0
O_2	3.20	2.35	3.57

Fortunately, this new composite structure functioned as permeable mixed matrix membrane. Permeability values of pure PAEK and PPy filler loaded membranes are presented in Table 4.3.1. One of the most interesting result was the constant N_2 permeability with changing filler load. In the previous study [65] with polycarbonate and chemically synthesized polypyrrole, it was reported that with increasing conductive filler loading almost constant N_2 permeability was recorded. This may be because of compact composite structure occurring by addition of same sort of PPy which may be confirmed by the SEM micrographs. As a general trend, as loading increases permeability values increases; however the membrane with 10% PPy filler loading reveals interesting behavior since there are permeability decreases observed instead of expected increases. Tighter structure of 10 % PPy loaded membranes may the reason for this decrease. The PPy powder particles may hinder the free diffusion by blocking the gas channels. At load of 10% PPy, Ar, O_2 and H_2 gases comply with this explanation. Above this load, because of the possible disorder in the structure, permeability for these gases increased again. Apart from Ar, O_2 and H_2 gases, permeability of CO_2 increased as PPy load increases. However, very slight increase was observed in 10 % PPy load which supports previous comments. As known CO_2 has a strong plastization effect on polymeric materials. It may be speculated that the existence of PPy may enhance this plastization of mixed matrix structure and make the permeability value increase. Affinity for like dissolves like interaction, may be valid for CH_4 and organic structures on polymer surface since permeability values of CH_4 increased directly with increasing PPy load. Comparing to the results of same kind of study with a different polymer matrix PC [65], it can be reported that PAEK forms a more permeable structure with PPy.

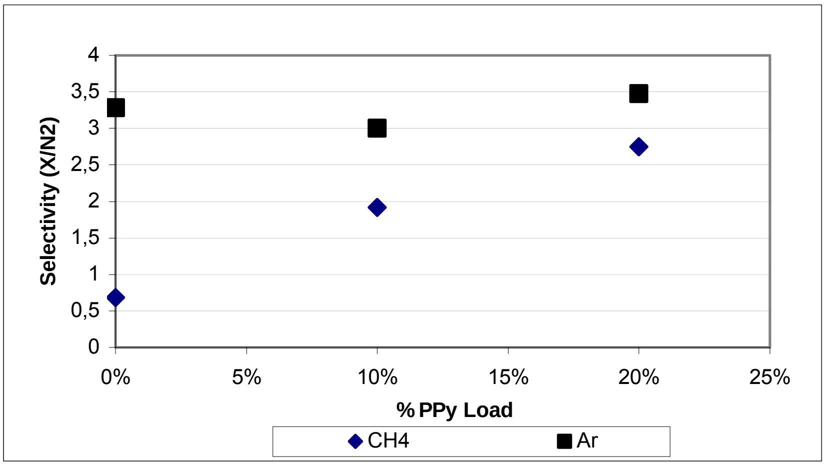


Figure 4.3.1.1 Selectivity data of CH_4 and Ar for PAEK-PPy Mixed Matrix Membranes at different PPy load

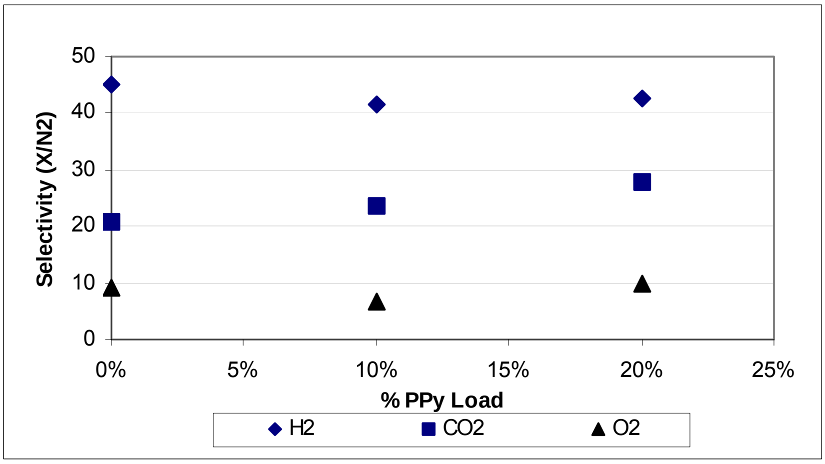


Figure 4.3.1.2 Selectivity data of H_2, CO_2 and O_2 for PAEK-PPy Mixed Matrix Membranes at different PPy load

In Figure 4.3.1.1 and Figure 4.3.1.2 the ideal selectivity values are graphed for PPy loaded PAEK membranes. Constant N_2 permeability would favor the permselectivity of other gases much more. However, permeability loss in 10% filler load for all gases, except CO_2 and CH_4, also causes a loss in selectivity. Linearly increasing permeability of CO_2 and CH_4, which was previously explained, causes a direct increase in selectivity. This also affects the selectivity based on the industrially important gas pairs, CO_2/CH_4, H_2/CH_4 and O_2/N_2. For 10 % PPy filler loaded membranes these selectivities were reported as 12.32, 21.59 and 6.53 respectively. Selectivity values for the same gas pairs at 20 % PPy filler load were recorded as 10.16, 15.5 and 9.91 respectively. As seen, while permeability increase both for CO_2 and CH_4 was affecting the selectivity values slightly negatively for CO_2/CH_4, H_2/CH_4 pairs, and O_2 gas selectivity increases from 6.53 to 9.91.

4.3.2 Investigation of Membrane Morphology

The SEM images of the surfaces and cross-sections of both pure PAEK membranes and PAEK-PPy mixed matrix membranes with chemically synthesized polypyrrole fillers are shown in following figures 4.3.2.1-4.3.2.6 with respect to the increasing loading (10%-30%).

Stiff chemical structure of PAEK causes a dense physical structure which is clearly seen in Figure 4.3.2.1. When the scanning electron micrographs of pure PAEK (Figure 4.3.2.1) and PPy loaded membranes are compared, agglomerated polypyrrole particles are clearly seen with increasing loading (Figure 4.3.2.3 and Figure 4.3.2.4). The most interesting thing observed for the structures of membranes at 20% and above loadings is that, fillers combine together to form polypyrrole agglomerates when overlooked to the surface and create a cave-like structures around them. That type of structure is believed to arise from the partial incompatibility of PAEK chains and the chemically synthesized polypyrrole filler, implying that polypyrrole powder interacts more strongly with itself than the matrix polymer although both have a polymeric structure. At higher loadings (Figure 4.3.2.6), polypyrrole fillers and poly(arylene ether ketone) form a disordered complex structure. As discussed before 30% loaded membranes was not workable which may clearly seen from the cross-sectional SEM image in Figure 4.3.2.6. From the micrograph of 30% loading (Figure-4.3.2.6), it is clearly seen that the cavities around the polypyrrole moieties provide an alternate path resulting in the loss of the selectivity at this loading. This kind of behavior was also observed with other mixed matrix membranes [57, 59, 61]; but in these studies zeolites were used as fillers and zeolite openings created a continuous channel network at higher loadings resulting higher permeation rates.

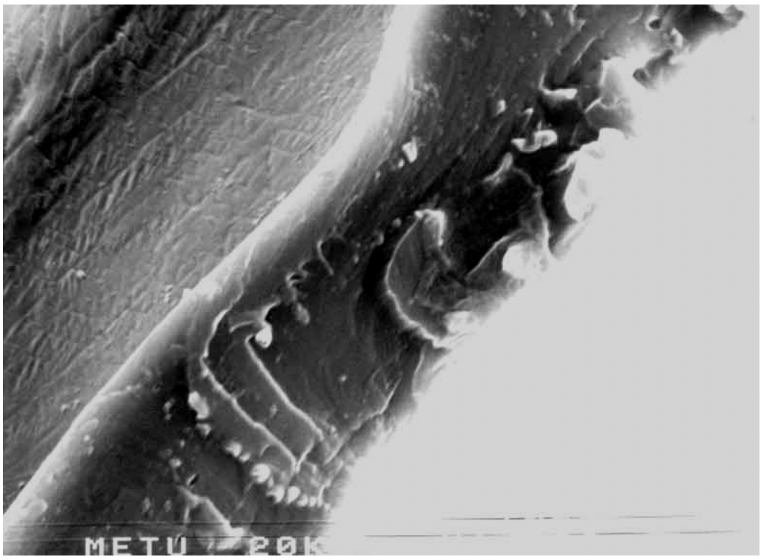


Figure 4.3.2.1 The Micrograph of Pure PAEK membrane
(Cross-sectional View x 1500)

It is believed that a small amount of PPy powder particles may hinder the free diffusion by blocking the gas channels; thus more compact, tight and less permeable structure forms at this load. One other point is skin layer which can be observed in cross-sectional views of 10% PPy loaded PAEK membranes (Figure 4.3.2.2). This thin layer may convert the membrane to asymmetric membrane which may be the reason of compact structure resulting less permeable membranes at this load.

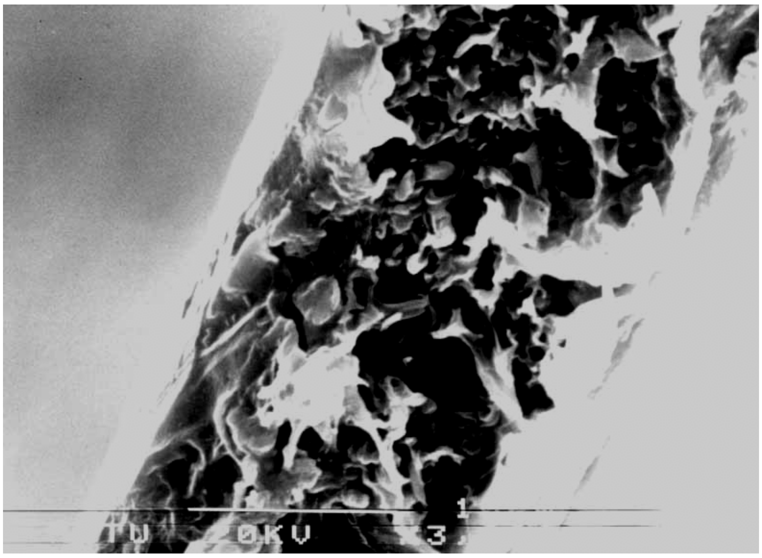


Figure 4.3.2.2 The Micrograph of 10% PPy filler loaded PAEK-PPy mixed matrix membrane (Cross-sectional View x 3000)

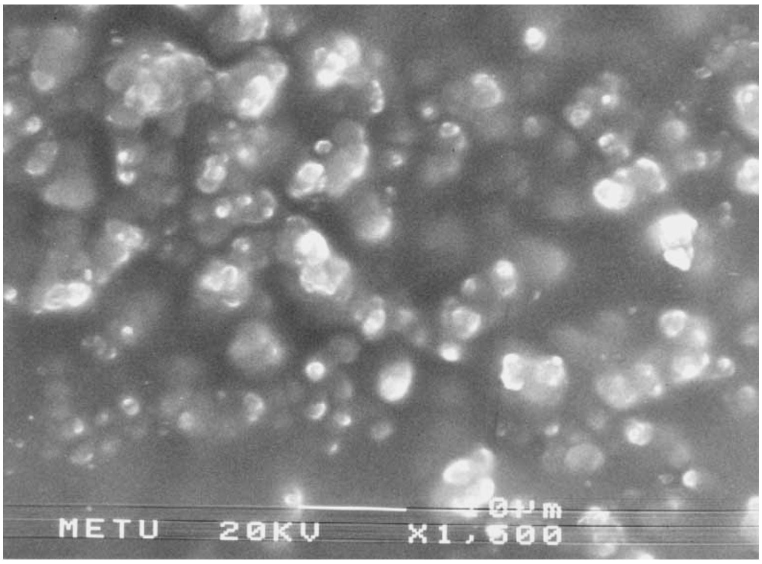


Figure 4.3.2.3 The Micrograph of 10% PPy filler loaded PAEK-PPy mixed matrix membrane (Surface View x 1500)

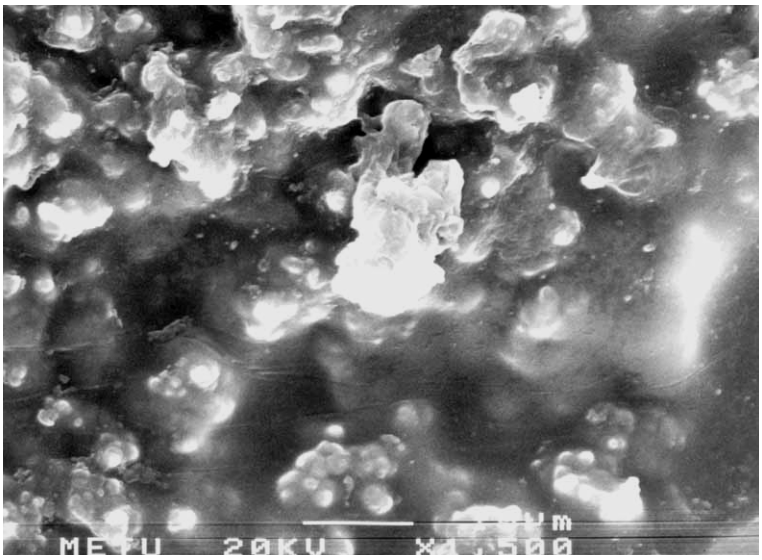


Figure 4.3.2.4 The Micrograph of 20% PPy filler loaded PAEK-PPy mixed matrix membrane (SurfaceView x 1500)

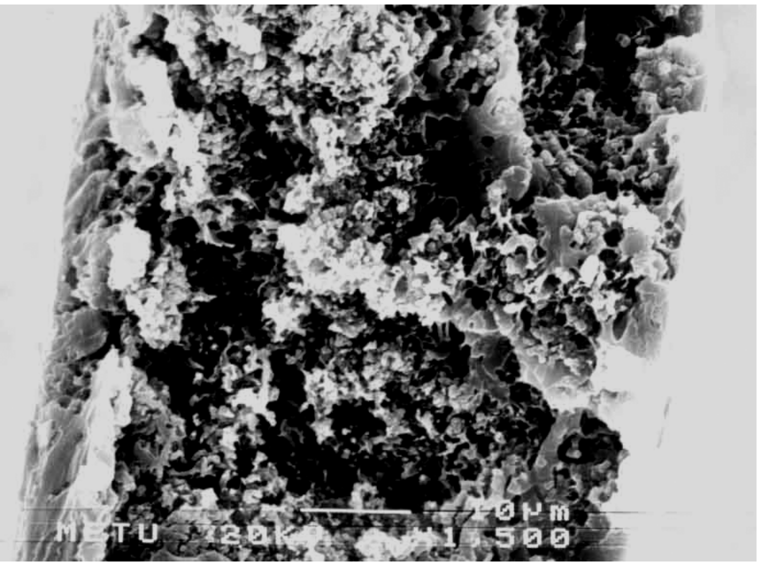


Figure 4.3.2.5 The Micrograph of 20% PPy filler loaded PAEK-PPy mixed matrix membrane (Cross-sectional View x 1500)

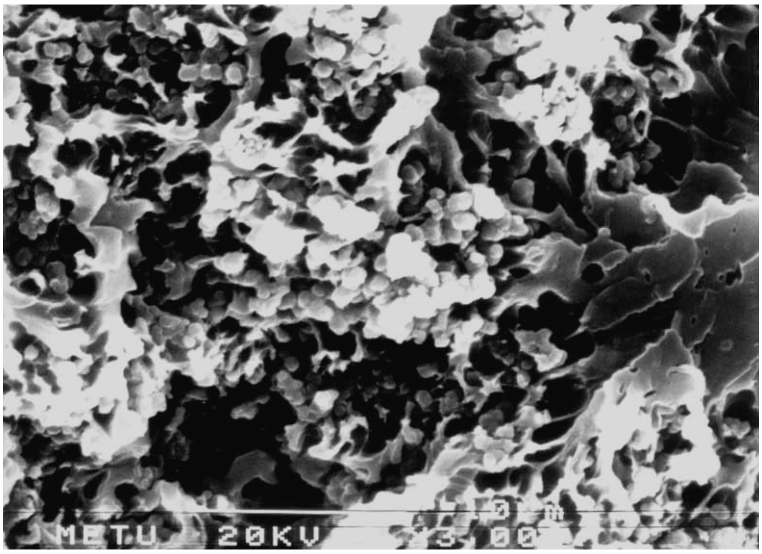


Figure 4.3.2.6 The Micrograph of 30% PPy filler loaded PAEK-PPy mixed matrix membrane (Cross-sectional View x 3000)

The cave-like voids and this thin skin structure may also have counter effects on permeability, so this might be another reason for less permeability at low loads of filler. According to this explanation, low amount of PPy, which is responsible for cave-like voids and more permeable structure, affects less than skin layer, which slows down the permeation. In Figure 4.3.2.2, it is clearly observed that thin PAEK skin layer covers the composite structure of 10% PPy load. However at higher loads, the agglomerated polypyrrole particles damage this skin layer and cause loose in asymmetric membrane structure resulting high permeabilities. In Figure 4.3.2.5 skin layer is also recognizable, but previous surface view of the same membrane explains the deformed structure of this layer (Figure 4.3.2.4)

Finally from the cross-section micrographs, clusters of polypyrrole powder are seen just under the PAEK as if a pillow under a blanket. These micrographs also imply a random homogeneous distribution of group of polypyrrole powder in the matrix.

CHAPTER 5

CONCLUSION

5.1 Conclusions regarding the Performance of Dense Homogeneous PAEK membranes

- PAEK is quite hopeful for future studies of gas separation membranes due to both its good mechanical properties and gas separation performance. PAEK membranes showed promising selectivity with enough permeability performance.
- Permeability coefficients of PAEK increased as temperature increases as expected for glassy polymers.
- As temperature increases selectivity values stayed almost constant which is an important property for industrial applications at high temperatures.
- Solution-Diffusion mechanism and Arrhenius law is valid for PAEK membranes. However, there are not worthy variations of activation energies because quite stiff chemical structure of PAEK keeps the permeation activation energies of all gases very close to each other.

5.2 Conclusions on the Performance of PAEK-PPy Mixed Matrix Membranes

- PAEK and PPy forms a composite structure which can be cast as permselective gas separation membranes.
- The mixed matrix membranes of PPy with PAEK showed lower permeabilities compare to pure PAEK films which signifies compatible composite structure of PPy and PAEK at low filler load.
- At low PPy filler loads, the PPy powder particles may hinder the free diffusion by blocking the gas channels which results low permeable and selective membrane. The packed structures of the membrane matrix at low loadings are observed through SEM micrographs
- At high PPy filler loads, the cave-like voids between polypyrrole moieties and PAEK matrix due to the partial incompatibility of polymers can easily be observed. By this way, an alternate path for gas molecules may be formed which results in the loss of selectivities.
- With a careful observation, very thin skin layer covering the membrane surface was determined. With this layer, membrane may act as an asymmetric structure implying lower permeabilities but higher selectivities in composite membrane. There may be a counter effect between this skin layer and cave-like voids; as PPy load increases, the low permeation effect of skin layer becomes insufficient. Therefore, especially at lower loads of filler this skin layer can function properly.
- In order to improve membrane performance, different types of conducting fillers can be introduced in to PAEK matrix as a future study. On the other hand, to improve the compatibility of insulating polymer-conducting polymer pair, organic compatibilizers can be added to the structure to develop high performance conducting filler loaded mixed matrix membranes.

LIST OF PUBLICATIONS

- G. Mergen, L. Toppare, L. Yılmaz, ‘Gas Permeation Properties of Hexafluorobisphenol A based poly(arylene ether ketone) and Its Mixed Matrix Membranes with Polypyrrole’, in preparation

REFERENCES

[1] R.W. Spillman, M.B. Sherwin, 'Gas Separation Membranes: The First Decade', Chemtech., (1990) 378-384

[2] A.K. Fritzsche, R.S. Narayan, 'Gas Separation By Membrane Systems', Chem. Econ. & Eng. Rev., 19 (1987) 19-31

[3] E.S. Peterson, M.L. Stone, R.R. McCaffi-ey and D.G. Cummings, Mixed Gas Separation Properties of Phosphazane Polymer Membranes, Separation Science and Tech., 28 (1993), (1-3) 423-440.

[4] S.A. Stern, 'Polymer for Gas Separations: The Next Decade', J. of Memb. Sci., 94 (1994) 1-65

[5] R. Field, P. Gallagler, R. Hughes, A,J. Merry, K. Scott, 'Industrial Membrane Separation Technology', Blackie Academic & Professional, London, (1996)

[6] W.E. Price, C.O. Too, G.G. Wallace and D. Zhou 'Development of Memebrane Systems based on Conducting Polymers', Synthetic Metals 102 (1999) 1338-1341

[7] H.R. Alcock, W.J. Koros, 'Gas Permeation and Selectivity of Poly(organophosphazane) Membranes', Macromolecules, 26 (1993) 1493-1502

[8] M. Moadded, W.J. Koros, 'Gas Transport Properties of Thin Polymeric Membranes in the Presence of Silicon Dioxide Particles', J. of Memb. Sci., 125 (1997) 141-149

[9] M.E. Rezac, N.S. Moore, E. T. Sorensen, 'Polymer Tg versus Upper-use Temperature for Membranes : How Do They Compare', Abstract: 77e. (1996 Spring) Meeting, New Orleans, LA.

[10] W.J. Koros, M.R. Coleman, R.B.Walker, ‘Controlled Permeability Polymer Membranes’, Annu. Rev. Mater. Sci., 22 (1992) 47-89.

[11] B.D. Freeman, ‘Basis of Permeability/Selectivity Trade off Relations in Polymeric Gas Separation Membranes’ Macromolecules, 32 (1999) 375-380

[12] M. R. Anderson, B.R. Mattes, H. Reiss, R. B. Kaner, ‘Conjugated Polymer Films for Gas Separations’, Science, 252 (1991) 1412-1415

[13] R. V. Parthasarathy, V. P. Menon, C. R. Martin, ‘Unusual Gas Transport Selectivity in a Partially Oxidized Form of the Conductive Polymer Polypyrrole’, Chem. Mater., 9 (1997) 560-566

[14] J. Rodriquez, H. J. Grande, T. F. Otero, ‘Handbook of Organic Conductive Molecules and Polymers: Vol 2 Conductive Polymers: Synthesis and Electrical Properties’, John Wiley & Sons, (1997)

[15] M. Mulder, ‘Basic Principles of Membrane Technology’, Kluwer Academic Publishers, (1991)

[16] S. Kumar, J. N. Shah, S. B. Sawant, J. B. Joshi, V. G. Pangankar, ‘Permeation in Filled Membranes: Role of Solute-Filler Interactions’, J. Memb. Sci., 134 (1997) 225-233

[17] H. Winston, K. Sirkar, ‘Membrane Handbook’, Chapman & Hall Ed., New York, 1992, 19-94

[18] R. Singh, ‘Industrial Membrane Separation Processes’, Chemtech., (1998) 33-44

[19] D.G. Pye, H.H. Hoehn, ‘Measurement of Gas Permeability of Polymers II: Apparatus for Determination of Permeabilities of Mixed Gases and Vapors’, J. Appl. Polym. Sci., 22 (1976) 287

[20] L. M. Robeson, W.F. Burgoyne, M. Langsam, A.C. Savoca, C. F. Tien, ‘Correlation of Separation Factor versus Permeability for Polymeric Membranes’, Polymer, 35 (1994) 497

[21] L.M. Robeson, ‘Polymer Membranes for Gas Separation’ Current Opinion in Solid State & Material Sci., 4 (1999) 549-552

[22] M. Moe, W. J. Koros, H.H. Hoehn, G.R. Husk, 'Effects of Film History on Gas Transport in a Fluorinated Aromatic Polyimide', J.Appl. Polym. Sci., 36 (1988) 1833-1846

[23] H.H. Hoehn, 'Aromatic Polyimide Membranes', ACS Symp. Ser., 269 (1985) 81-98

[24] L. M. Costello, W.J. Koros, 'Effect of Structure on The Temperature Dependence of Gas Transport and Sorption in a Series of Polycarbonates' Journal of Polym. Sci. Part B: Polymer Physics, 32 (1994) 701-713

[25] K.E. Min, D.R. Paul, 'Effects of Tacticity on Permeation Properties of Poly(methyl methacrylate)', J Polym. Sci : Part B: Polym. Phys. Ed., 26 (1988) 1021-1033

[26] S.A. Stem, V.M. Shah, B.J. Hardy, 'Structure-Permeability Relationships in Silicone Polymers', J. Polym. Sci., Polym. Phys. Ed., 27 (1987) 887

[27] S.A. Stem, H. Yamamato, 'Structure /Permeability Relationship of Polyimide Membranes: Applications to the Separation of Gas Mixtures', J. Polym. Sci.: Part B: Polym. Phys. Ed., 27 (1989) 1887-1909

[28] M. Langsam, W.F. Burgoyne, 'Effects of Diamine Monomer Structure on the Gas Permeability of Polyimides I. Bridged Diamines', J. Polym. Sci. Part A: Polym. Chem. Ed., 31 (1993) 909-921

[29] Y. Hirayama et al, 'Relation of Gas Permeability With Structure of Aromatic Polyimides I., J. Membr. Sci., 111 (1996) 169-182.

[30] Y. Hirayama et al, 'Relation of Gas Permeability With Structure of Aromatic Polyimides II., J. Membr. Sci., 111 (1996) 183-192.

[31] J. Lianda, Xu Jiping, 'A Simple Method for Prediction of Gas Permeability of Polymers from Their Molecular Structure', Polymer Journal, 23-No. 5 (1991), 417-425

[32] W. J. Koros, G. K. Fleming, 'Membrane Based Gas Separation', J. Memb. Sci., 83 (1993) 1-80

[33] F. Selampınar, PhD Thesis, 'Conducting Polymers and Composites of Polymers of Polypyrrole and Their Uses as Sensors' , METU, October 1997

[34] R.M. Johnson, Encyl. Polym. Sci. Technol., 11 (1969) 447

[35] R.B. Seynour and G.S. Kirshenbaum, 'High Performance Polymers: Their Origin and Development', Elsevier, (1986)

[36] I. Fukawa, T. Tanabe, 'Peraration of Dibenzofuran-Type Amorphous Polytherketone by Novel Etherification Reaction', J. Polym.Sci.: Part A: Polymer Chemistry, 30 (1992) 1977-1985

[37] Y. Bourgeois, Y. Charlier, J. Devaux and R. Legras, 'Synthesis of Poly(aryl ether sulfone)-Poly(aryl ether ketone) Triblock Copolymer', Polymer, 37 No:24 (1996) 5503-5511

[38] F.W. Mercer, A. Easteal, M. Bruma, 'Synthesis and Properties of New Alternating Poly(aryl ether) Copolymers Containing Cyano Groups', Polymer, 38 No:3 (1997) 707-714

[39] F.W. Mercer, M.M. Fone, V.N. Reddy, A.A. Goodwin, 'Synthesis and Characterization of Fluorinated Polyetherketones Prepared from Decafluorobenzophenone', Polymer, 38 No:8 (1997) 1989-1995

[40] F. Selampinar, U. Akbulut, E. Yildiz, A. Güngör, L. Toppare, 'Synthesis of a Novel Poly(arylene ether ketone) and its Conducting Composites with Polypyrrole', Synthetic Metals 89 (1997) 111-117

[41] F.P. Galtz, R. Mülhaupt, J.D. Schultze, J. Springer, 'Gas Permeabilities of Amorphous segmented 6F Poly(arylene thioether imide)s and Corresponding Poly(arylene sulfone imide)s', J. Memb. Sci. 90 (1994) 151-159

[42] J.M. Mohr, D.R. Paul, G.L. Tullos, P.E. Cassidy, 'Gas Transport Properties of Poly(ether ketone) Polymers', Polymer 32 No:13 (1991) 2387-2394

[43] C.L. Aitken, D.R. Paul, D.K. Mohanty, 'Gas Transport Properties of Poly(arylether bissufone)s and Poly(arylether bisketone)s', J. Polym. Sci.: Part B: Polymer Physics, 31 (1993) 983-989

[44] G. Maier, M. Wolf, M. Bleha, Z. Pientka, 'Gas Permeabilities of Polymers with Indan Groups in the Main Chain. 1 Poly(ether ketone)s', J. Memb. Sci. 143 (1997) 105-113

[45] Z.Y. Wang, P.R. Mouliné, Y.P. Handa, ‘Gas Transport Properties of Novel Poly(arylene ether ketone)s Containing Dibenzoylbiphenyl and benzonaphthanone Moities’, J. Polym. Sci.: Part B: Polymer Physics, 36 (1998) 425-431

[46] Zhi-Kang Xu, C. Dannenberg, J. Springer, S. Banerjee, G. Maier, ‘Novel Poly(arylene ether) as Membranes for Gas Separation’, J. Memb. Sci. 205 (2002) 23-31

[47] Xin-Gui Li, M. Huang, I. Kresse, J. Springer, ‘ Gas Transport in Bisphenol A Poly(ether ether ketone ketone) Membrane’, Polymer 42 (2001) 8113-8124

[48] S. Açıkalın, MS Thesis, ‘Effect of Temperature on Gas Permeation Properties of Polymeric membranes’, METU, September 1996

[49] Kim Tae-Han, W.J. Koros and G.R. Husk, ‘Temperature Effects on Gas Permeation Properties in Hexafluoro Aromatic Polyimides’, J. Membr. Sci. 4 (1989) 43-56

[50] K. Haraya, Hwang Sun-Tak, ‘Penneation of O_2, Ar and N_2 Through Polymer Membranes’, J. Membr. Sci., 71 (1992) 13-27

[51] I. Pinnau, L.G. Toy, ‘Gas and Vapor Transport Properties of Amorphous Perflorinated Copolymer Membranes based on 2,2-bistriflouromethyl-4,5-diflouro-1,3-dioxole/tetrafluoroethylene’, J. Membr. Sci. 109(1996) 125-133

[52] H. Kamuzawa, J.-S. Wang, B. Naito, B. Messaoudi, E. Sada., ‘Gas Transport in Polymeric Membranes at Temperatures Above and Below Glass Transition Point’, J. Appl. Polym. Sci., 51 (1994) 1015-1020.

[53] T. Gürkan, N. Baç, G. Kıran, T. Gür, ‘A New Composite Membrane for Selective Transport of Gases’,J. Memb. Sci., 93 (1994) 283

[54] M. Jia, K. V. Peinemann, R.D. Behling, ‘Molecular Sieving effects of Zeolites Filled Silicone Rubber MembranesJ. Memb. Sci., 57 (1991) 289

[55] J. M. Duval, B.Folkers, M.H.Y. Mulder, C.A. Smolders, Ibid., 80 (1993) 189

[56] R.H.B. Bouma, A. Checchetti, G. Chidichimo, E. Drioli, ‘ Permeation through a Heterogeneous Membrane: The Effect of the Dispersed Phase’, J. Memb. Sci., 128 (1997) 141-149

[57] M. Tanioka, A. Gobayashi, Y.Kageyama, K. Miyasaki, K. Ishikawa, ‘Effects of Carbon Filler on Sorption and Diffusion Of Gases through Rubbery Materials’, J. Polym. Sci., 20 (1982) 2197-2208

[58] M.G. Süer, N. Baç., L. Yılmaz, ‘Gas Permeation Characteristics of Polymers-zeolite mixed matrix membranes’, J. Membr. Sci. 91 (1994) 77-86

[59] T. Battal, N. Baç, L. Yılmaz, ‘Effect of Feed Composition on the Performance of Polymer-Zeolite Mixed Matrix Gas Separation Membranes’, Sep. Sci. and Tech., 30 (1995) 2365-2384

[60] Y. Tsujita, ‘Membrane Science and Technology’, Y. Osada and T. Nakagawa Eds., Dekker, New York, (1992)

[61] Ş.B. Tantekin-Ersolmaz, L.Şenorkyan, N. Kalaonra, M. Tatlıer, A. Erdem-Şenatalar, ‘n-Pentane/I-pentane separation by using zeolite-PDMS mixed matrix membranes’, J. Memb. Sci., 189 (2001) 59-67

[62] H.H. Yong, H. C.Park, Y.S. Kang, J. Won, W.N.Kim, ‘Zeolite-filled polyimide membrane containing 2,4,6-triaminopyrimidine’, J. Memb. Sci., 188 (2001) 151-163

[63] D.Gülşen, P. Hacarlıoglu, L.Toppare, L. Yılmaz, ‘Effect of Preparation Parameters on the Performance of Conductive Composite Gas Separation Membranes’, J. Memb. Sci., 182 (2001) 29-39

[64] P. Hacarlıoğlu, MS Thesis, ‘Effect of Preparation Parameters on Performance of Dense Homogenous Polycarbonate and Polypyrrole-Polycarbonate Mixed Matrix Membranes’, METU, July 2001

[65] P. Hacarlıoğlu, L. Toppare, L. Yılmaz, ‘Conductive Polycarbonate-Polypyrrole Mixed Matrix Gas Separation Membranes’ J. Memb. Sci. Submitted 2002

[66] J. E. Frommer, R.R. Chance, 'Electrically Conductive Polymers', Encyclopedia of Polymer Science and Engineering, V5, 2nd Ed., John Wiley& Sons, (1986)

[67] S. Kuwabata, C.R. Martin, 'Investigation of the Gas Transport Properties of Polyaniline', J. Memb. Sci., 91 (1994) 1-12

[68] L. Rebattet, M. Escoubes, E. Genies, M. Pineri, 'Effect of Doping Treatment on Gas Transport Properties and on Separation Factors of Polyaniline Membranes', J. Appl. Polym. Sci., 57 (1995) 1595-1604

[69] B.R. Mattes, M.R. Anderson, J.A. Conklin, H. Reiss, R.B. Kaner, 'Morphological Modification of Polyaniline films for the Separation of Gases', Synth. Met., 55-57 (1993)

[70] L. Rebattet, M. Escoubes, E. Genies, M. Pieri, 'Sorption and Interactions of Gases in Polyaniline Powders of Different Doping Levels', J.Appl. Polym. Sci., 58 (1995) 923-932

[71] H. L. Wang, B.R. Mattes, 'Gas Transport and Sorption in Polyaniline Thin Film', Synth. Met., 102 (1999) 1333-1334

[72] C.R. Martin, W. Liang, V. Menon, R. Parthasarathy, A. Parthasarathy, 'Electronically Conductive Polymers as Chemically-Selective Layers for Membrane Based Separations', Synth. Met., 55-57 (1993) 3766-3773

[73] K. Kamada, J. Kamo, A. Motonaga, T. Iwasaki, H. Hosokawa, 'Gas Permeation Properties of Conducting Polymer:/Porous Media Composite Membranes I', Polym., 26 (1994) 141-149

[74] I.H. Musselman, L.Li, L. Washman, D. Varadarajan, S.J. Riley, M. Himyene, J.D. Ferraris, K.J. Balkus, 'Poly(3-dodecylthiophene) Membranes for Gas Separations', J. Memb. Sci., 152 (1999) 1-18

[75] B.D. Reid, V.H.M. Ebron. I.H. Musselman, J.P. Ferraris, K.J. Balkus Jr., 'Enhanced gas selectivity in Thin Film Composite Membranes of Poly(3-(2-acetoxyethyl)thiophene)' J. Memb. Sci., 195 (2002) 181-192

[76] J.C. Thiéblemont, M.F. Planche, C. Perescu, J.M. Bouver and G. Bidan, 'Stability of Chemically synthesized Polypyrrole Films', Synthetic Metals, 59 (1993) 81-96

[77] T. Battal, MS Thesis, 'Separation of Binary Gas Mixtures with Zeolite-Polymer Mixed Matrix Membranes', METU, 1994

APPENDIX

A- Reproducibility Experiments

DATA TABLES OF TEMPERATURE EXPERIMENTS

25 C

	1st cast of PAEK			2nd cast of PAEK			3rd cast of PAEK		
#of Runs (Perm)	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
N2	0,35	0,35	0,35	0,36	0,37	0,34	0,34	0,34	0,36
CH4	0,24	0,24	0,25	0,23	0,24	0,25	0,24	0,25	0,25
Ar	1,13	1,15	1,19	1,11	1,17	1,2	1,13	1,15	1,13
H2	15,8	15,9	17	14,6	16	15,9	15,2	15,5	16
CO2	7,4	7,5	7,4	7,2	7,4	7,5	6,8	6,9	7,5
O2	3,3	3,2	3,16	3,11	3,21	3,3	3,2	3,2	3,14

50 C

	1st cast of PAEK			2nd cast of PAEK			3rd cast of PAEK		
#of Runs (Perm)	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
N2	0,72	0,73	0,72	0,74	0,73	0,72	0,72	0,73	0,7
CH4	0,63	0,62	0,63	0,63	0,63	0,64	0,6	0,63	0,62
Ar	1,83	2,01	1,97	1,84	1,9	2,1	2	2,1	1,98
H2	37,2	37,5	38,5	36,8	37,1	37,6	37,1	38,2	38,5
CO2	13,1	14	13,9	14,2	13,8	14,1	13,8	14,1	13,7
O2	5,6	5,8	5,85	5,71	5,89	5,9	5,96	5,9	6,2

70 C

	1st cast of PAEK			2nd cast of PAEK			3rd cast of PAEK		
#of Runs (Perm)	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
N2	1,58	1,65	1,63	1,71	1,67	1,7	1,63	1,65	1,65
CH4	0,97	1,2	0,88	0,98	1,01	1,03	0,88	0,95	0,98
Ar	3,12	3,2	3,11	3,1	3,17	3,15	3,07	3,13	3,15
H2	57,6	55,4	59,2	58,1	58	59	56,2	56,9	58
CO2	19,2	20,2	19,1	18,8	19,3	19,5	19	18,6	19,5
O2	6,79	7,35	7,1	6,93	7,2	6,86	6,88	6,93	7,02

85 C

	1st cast of PAEK			2nd cast of PAEK			3rd cast of PAEK		
#of Runs (Perm)	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
N2	1,86	1,88	1,85	1,85	1,87	1,85	1,86	1,84	1,87
CH4	1,62	1,6	1,65	1,59	1,62	1,64	1,6	1,63	1,6
Ar	3,75	3,8	3,7	3,7	3,72	3,75	3,76	3,75	3,65
H2	73	74	73	75	74	75	74	73	72
CO2	26,3	25,6	26,1	26,2	26,5	26,6	26,1	25,7	26,6
O2	11,1	10,9	11,2	11,2	10,6	11	11,2	11,1	11,2

Stability of Permeability values of Pure PAEK for each run at 25 °C

#of Runs	1st	2nd	3rd	4th	5th	6th	7th	8th	9th
N2	0,35	0,35	0,35	0,36	0,37	0,34	0,34	0,34	0,36
CH4	0,24	0,24	0,25	0,23	0,24	0,25	0,28	0,25	0,27
Ar	1,19	1,15	1,13	1,2	1,17	1,11	1,19	1,15	1,13
H2	14	15	14	14	16	13	14	15	14
CO2	7,4	6,3	6,8	7,2	6,8	7	7,1	6,9	6,4
O2	3,3	3,2	3,16	3,11	3,21	3,3	3,2	3,2	3,14

B- Arrhenius Calculations

Data for Arrhenius Plots of Gasses through Paek(6F-BisA) Membrane

	1/298K	**1/313K**	**1/343K**	**1/358K**
	0,0034	0,0031	0,0029	0,0028
N_2	-24,08	-23,35	-22,53	-22,41
CH_4	-24,45	-23,49	-23,06	-22,54
Ar	-22,89	-22,35	-21,89	-21,7
H_2	-20,27	-19,4	-18,97	-18,74
CO_2	-21,04	-20,39	-20,07	-19,76
O_2	-21,86	-21,26	-21,08	-20,62

ln P= ln Po - (Ep/RT) ; (R=8,314j/mol.K)

	Ln Po intersept	**Ep/R** Slope	**Ep** (J/mol)	Kcal/mol		**Ln Po** intersept	**Ep/R** slope	**Ep** (J/mol)	Kcal/mol
N_2	13,93	-2989	**24849**	**5,939**	**H_2**	11,65	-2511	**20874**	**4,989**
CH_4	14,05	-3045	**25318**	**6,051**	**CO_2**	13,98	-2067	**17183**	**4,107**
Ar	16	-2025	**16834**	**4,023**	**O_2**	15,37	-1903	**15822**	**3,781**