DEVELOPMENT OF PBI BASED MEMBRANES FOR H_2/CO_2 SEPARATION

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ABSTRACT

DEVELOPMENT OF PBI BASED MEMBRANES FOR H_2/CO_2 SEPARATION

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Recent developments have confirmed that in the future hydrogen demand in industrial applications will arise because of the growing requirements for H_2 in chemical manufacturing, petroleum refining, and the newly emerging clean energy concepts. Hydrogen is mainly produced from the steam reforming of natural gas and water gas shift reactions. The major products of these processes are hydrogen and carbon dioxide. The selective removal of CO_2 from the product gas is important because it poisons catalysts in the reactor and it is highly corrosive. Membrane separation processes for hydrogen purification may be employed as alternative for conventional methods such as adsorption, cryogenic distillation.

Mixed matrix membranes (MMMs) are composed of an insoluble phase dispersed homogeneously in a continuous polymer matrix. They have potential in gas separation applications by combining the advantageous properties of both phases. The objective of this study is to produce neat polybenzimidazole (PBI) membranes and PBI based mixed matrix membranes for separation of H_2/CO_2. Furthermore, to test the gas permeation performance of the prepared membranes at permeation temperatures of 35^oC to 90^oC.

Commercial PBI supplied from both Celanese and FumaTech were used as polymer matrix. PBI was selected based on its thermal, chemical stabilities and mechanical properties and its performance as a fuel-cell membrane produced by PBI.
Micro-sized Zeolite 3A and nano-sized SAPO-34 are zeolites with 0.30 nm and 0.38 nm pore size respectively have attracted considerable interest and employed as fillers in this study. Commercial Zeolite 3A and synthesized SAPO-34 by our group was used throughout the study. Membranes were prepared using N,N-dimethylacetamide as the solvent. Prepared membranes were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The effect of annealing procedure and operating temperature on gas separation performance of resultant neat PBI, PBI/Zeolite 3A and PBI/SAPO-34 membranes were investigated by gas permeation tests. Hydrogen and carbon dioxide gases were used for single gas permeation measurements. Two different annealing strategies were utilized namely in-line annealing and in-oven annealing. In-oven annealing was performed in an oven in nitrogen atmosphere at 120^oC, 0.7 atm while in-line annealing was performed in the gas permeation set-up by feeding helium as permeating gas at 90^oC and 3 bar.

Neat PBI and PBI/ Zeolite 3A membranes were in-oven annealed. The in-oven annealed membranes showed better selectivities with lower permeabilities, but the performance results of these membranes had low repeatability. On the other hand, in-line annealed membranes showed much higher permeabilities and lower selectivities with stable performance. By changing the annealing method hydrogen permeability increased from 5.16 Barrer to almost 7.77 barrer for neat membranes and for PBI/Zeolite 3A mixed matrix membranes increased from 5.55 to to 7.69 Barrer at 35°C. The selectivities were decreased from 6.21 to 2.31 for neat membranes and for PBI/Zeolite 3A from 5.55 to 2.63.

Effect of increasing operating temperature was investigated by using in-line annealed membranes. Increasing temperature from 35°C to 90° improved the performance of the both types of membranes and repeatable results were obtained. Besides neat PBI and PBI/Zeolite 3A, PBI/SAPO-34 membranes were prepared only via in-line annealing. The addition of nano-sized filer to the membranes provided homogeneous distribution in polymer matrix for PBI/SAPO-34 membranes. For this type of membrane hydrogen permeability increased from 8.01 to 26.73 Barrer and with no change in H_2/CO_2 selectivities via rising temperature. Consequently, it is better to study hydrogen and carbon dioxide separation at high temperature.

For all types of membranes hydrogen showed higher activation energies. In between all membranes magnitude of activation energies were the highest for PBI/SAPO-34 membrane which is an indication of good interaction between polymer and zeolite interface. In-line annealed membranes gave the best gas permeation results by providing repeatability of measurements. Among all studied membranes in-line annealed PBI/SAPO-34 membrane exhibited the best gas permeation results.

Keywords: Mixed Matrix Membranes, Gas Separation, PBI

ÖZ

H_2/CO_2 AYIRIMI İÇİN PBI BAZLI MEMBRANLARIN GELİŞTİRİLMESİ

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En son gelişmeler kimyasal üretim, petrolün damıtılması ve yeni geliştirilen temiz enerji konseptlerinde artan ihtiyaçtan dolayı gelecekte sanayi uygulamalarında hidrojene olan talebin artacağını göstermektedir. Hidrojen başlıca buhar dönüşüm prosesi ve su gaz dönüşüm reaksiyonlarından üretilir. Bu proseslerin ana ürünleri hidrojen ve karbondioksittir. Karbondioksitin oldukça korozif oluşu ve reaktörde bulunan katalizörleri zehirlediği için seçici olarak uzaklaştırılması önemlidir. Hidrojen saflaşlaştırma işlemi için membranlar; adsorpsiyon, kriyojenik distilasyon gibi geleneksel metotlar yerine kullanılabilinir.

Karışık matrisli membranlar, devamlı bir polimer matrisi içerisine çözünmeyen bir fazın homojen olarak dağıtılması ile oluşur. Bu membranlar her iki fazın avantajlı özelliklerini birleştirerek gaz ayırımında kullanılabilme potansiyeline sahiptirler. Bu çalışmanın amacı H_2/CO_2 ayırımı için polibenzimidazol (PBI) ve PBI bazlı karışık matrisli membranları üretmek ve aynı zamanda üretilen bu membranların gaz ayırım performanslarının 35^{o}C ve 90^{o}C aralığında test etmektir.

Ticari olarak hem Celanese hem de FumaTech firmalarından temin edilen PBI, polimer matrisi olarak kullanılmıştır. PBI sahip olduğu termal, kimyasal stabilite ve mekanik özellikleri ve yakıt-pili membranı üretiminde kullanıldığında membran olarak gösterdiği performansı baz alınarak seçilmiştir.

Sırasıyla 0.30 nm ve 0.38 nm gözenek çapına sahip mikro boyutlu Zeolit 3A ve nano boyutlu SAPO-34 önemli ölçüde dikkat çekmiştir ve bu çalışmada dolgu malzemesi olarak kullanılmıştır. Ticari Zeolite 3A ve grubumuz tarafından sentezlenmiş olan SAPO-34 çalışma boyunca kullanılmıştır. Hazırlanan membranlar taramalı elektron mikroskobu (SEM), farklı taramalı kalorimetre (DSC) ve termal gravimetrik analiz (TGA) ile karakterize edilmiştir. Hazırlanan PBI, PBI/Zeolit 3A ve PBI/SAPO-34 membranları ile gaz geçirgenlik testleri yapılarak tavlama prosedürünün ve çalışma sıcaklığının gaz geçirgenliğine etkisi araştırılmıştır. Hidrojen ve karbon dioksit tek gaz geçirgenlik ölçümleri için kullanılmıştır. Doğrudan tavlama ve fırında tavlama olarak tanımlanan iki farklı tavlama stratejisi uygulanmıştır. Fırında tavlama işlemi fırın içerisinde 120^{o}C, 0,7 atmosferde, doğrudan tavlama işlemi ise gaz geçirgenliğinin test edildiği düzenek içerisinde 90^{o}C ve 3 bar basınçta helyum gazının beslenmesi ile gerçekleştirilmiştir.

PBI ve PBI/Zeolit 3A membranları fırında tavlanmıştır. Fırında tavlanan membranlar daha iyi seçicilik fakat daha düşük geçirgenlik göstermişlerdir. Diğer taraftan doğrudan tavlanan membranlar çok daha yüksek geçirgenlik ve düşük seçicilik ile birlikte stabil performans göstermişlerdir. Tavlama metodunun değiştirilmesi ile 35^{o}C'de PBI membranlar için hidrojen geçrigenliği 5.16 Barrer'den 7.77 Barrer'e, PBI/Zeolit 3A membranlar için ise 5.55 Barrer'den 7.69

Barrer yükselmiştir. Seçicilikler ise PBI membranlar için 6.21’den 2.31’e, PBI/Zeolit 3A membranlar için ise 5.55’ten 2.63’e düşmüştür.

İşletme sıcaklığının arttırılmasının etkisi doğrudan tavlanmış membranlar kullanılarak incelenmiştir. Sıcaklığın 35^{o}C’den 90^{o}C’ye arttırdığımızda her iki tip membranın da performansı iyileşmiştir. PBI ve PBI/Zeolit 3A membranları yanında PBI/SAPO-34 membranı sadece doğrudan tavlama yöntemi kullanılarak hazırlanmıştır. Nano boyutlu dolgu maddesinin eklenmesi PBI/SAPO-34 membranı için polimer matrisi içerisinde homojen dağılımın olmasını sağlamıştır. Bu membran tipi için hidrojen geçirgenliği artan sıcaklıkla birlikte 8.01 Barrer’den 26.73 Barrer’e çıkmıştır. H_2/CO_2 seçicilik değeri değişiklik göstermemiştir. Sonuç olarak, hidrojen ve karbondioksit ayrımında yüksek sıcaklıklarda çalışmak daha uygun olacaktır.

Bütün membran tipleri için hidrojen en yüksek aktivasyon enerjisi göstermiştir. Tüm membranlar arasında da her iki gaz için en yüksek aktivasyon enerjileri PBI/SAPO-34 membranı için elde edilmiştir, bu da polimer-zeolit ara yüzeyinin iyi etkileşmiş olduğunun bir göstergesidir. Doğrudan tavlanan membranların sonuçların tekrar edilebilirliğini sağlayarak iyi gaz geçirgenlik sonuçlarını vermişlerdir. Çalışma boyunca kullanılan membranlar arasında en iyi gaz geçirgenlik sonuçlarını PBI/SAPO-34 membranları ile elde edilmiştir.

Anahtar kelimeler: Karışık Matrisli Membran, Gaz Ayırımı, PBI

To My Dearest Family,

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A : Effective membrane area (cm^2)

D: Diffusivity (10^{-8} cm^2/s)

E_a : Activation energy of permeation (kJ/mol)

E_d: Activation energy of diffusion (kJ/mol)

H_s: Heat of sorption (kJ/mol)

J : Flux ($cm^3/cm^2.s$)

l: Thickness of the membranes (cm)

P : Permeability (Barrer)

R : Ideal gas constant

T : Temperature (°C)

Tg : Glass transition temperature (°C)

S: Solubility (cm^3 (STP)/cm^3.atm)

Greek Letters

α : Selectivity

Δp :Transmembrane pressure difference (cmHg)

Abbreviations

DMAc: N,N-dimethylacetamide

HMA : 2-hydroxy 5 methyl aniline

PDMS : Poly (dimethylsiloxane)

PES : Polyethersulfone

PBI : Polybenzimidazole

PBI-1 : PBI supplied from Celanese

PBI-2 : PBI supplied from FumaTeach

pNA : p-Nitroaniline

PTMSP : Poly (1-trimethylsily-1-propyne)

ZIF-8 : Zeolitic imidazolate framework-8

CHAPTER 1

INTRODUCTION

Today, in modern era most of the worldwide energy demand is provided by fossil fuels. Main challenge of using fossil fuels is its end products, mainly carbon dioxide, emission and their contribution to the greenhouse effect. Therefore developing new, sustainable and clean technologies became a major concern [1-3, 15-17]. Among several energy alternatives energy carrier hydrogen, which is a 'green' fuel, has gained a major interest [4]. Hydrogen, one of the essential materials in chemical industrial processes [18], can be generated from primary energy sources, natural gas (48%), coal (18%), oil (30%) [5], besides renewable energy sources, biomass, wind and solar can be used to produce [6].

Most commercially significant process which needs CO_2 removal is large-scale H_2 production via water gas shift reaction in coal gasification process operating at high temperatures and pressures.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \text{(SMR)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{(WGSR)}$$

This whole process consists of three main steps: catalytic reforming of methane (SMR), water gas shift reaction (WGSR) and finally hydrogen purification. Purification is required because hydrogen production comes up with CO_2 co-production, besides other trace amounts of H_2S, HCN, NH_3, heavy metals [20]. Hydrogen obtained by this method is an important input for processes like ammonia, urea, methanol, hydrochloric acid production and hydrodesulphurization and fuel cell applications [17-20]. Therefore, production of hydrogen at desired purities is essential for downstream applications.

Different approaches can be employed for hydrogen enrichment including conventional methods like pressure swing adsorption (PSA), temperature swing adsorption and cryogenic distillation. The most commonly used method is pressure swing adsorption. This method is based on adsorbent bed that purifies the inlet gas stream at high pressure. The adsorbents hold the impurities on its surface. Purified hydrogen is released from the top of the bed and impurities are expelled by depressurization. These cycles provides continuous purified product flow. Multiple pressure swing adsorption beds can be utilized for products with higher purities. Temperature swing adsorption is quite similar to PSA. But it needs time to heat and cool the adsorbents. Another alternative, cryogenic processes require very low temperatures to operate and relatively expensive. Those three commercial methods are energetically demanding operations. But all of them are relatively expensive and highly energy consuming methods compared to membrane separations [7].

The attractive properties of membrane processes are their simplicity, ease of operation and versatility to large number of potential uses. Hydrogen separation is suited to membrane technology as it has a very high permeation rate relative to most other gases [8, 9].

Materials used for membrane production cover a wide range from organic polymeric materials to inorganic materials (e.g. ceramics, oxides, etc.) and dense metals [10]. For gas separation, polymers become predominant materials because of their properties like easy processing, high mechanical stabilities, low operating cost and space requirements [11, 12].

Polymeric membranes are the types of membranes that are usually studied for gas separation [10-12]. The products of water gas shift reaction leave the reactor at high temperatures and pressures. Therefore, working with membranes produced from materials which can retain their mechanical and thermal stability at harsh operating conditions is the primary factor for this specific application. Polybenzimidazole (PBI), which was used in this study, has inherent mechanical, physical and chemical stability. This material retains its robustness up to 600-630^{o}C and has a high glass transition temperature (400-435^{o}C) [39, 63]. Furthermore, high chain packing density of this material provides diffusivity selectivity at temperatures above 150^{o}C. These properties and aliphatic group free structure make the polymer suitable for harsh operating conditions [48-50, 98].

For practical applications, it is important to produce polymeric membranes with suitable morphologies and enhanced gas separation performance. It is well known that polymeric membranes have a trade-off between the permeabilities and selectivities [53]. To surpass this limit and attain membranes, which are more feasible for commercial applications, as an alternative mixed matrix membranes containing zeolite fillers were produced. These two types of materials combine the prominent properties of both types of materials. Eventually, desired separation performances could be attained for particular separation [55-57].

If the aim is to obtain stable membranes at harsh industrial operating conditions, measuring the performance at only one temperature is not enough to fully elucidate the performance of a membrane. In industrial applications various temperatures are utilized and the performance of the membranes strongly affected by the temperature. Temperature dependent behavior of membrane toward gas transport should be investigated.

Within the scope of this study the effect of temperature and different annealing types on polymer and polymer-zeolite mixed matrix membranes were investigated. Polybenzimidazole was chosen as polymer matrix. Zeolite 3A and SAPO-34 particles incorporated mixed matrix membranes were produced and tested with hydrogen and carbon dioxide gases to see the influence of both temperature and annealing methodology on the membranes performances.

CHAPTER 2

LITERATURE SURVEY

In the last few decades energy efficient gas separation has become a significant issue. Different separation methods can be performed with regard to gases physical and chemical properties. The most important factor to determine the suitable method for any particular application is its process economics [13].

Membrane based gas separation compete with several traditional gas separation techniques. Commercialization of membranes and availability in the industrial applications can be possible by developing membranes which can operate at desired operating conditions with sufficient performance [14].

2.1 Gas Separation Membranes

Simply, membrane is a selective barrier between two phases. It can easily discriminate between molecules regarding difference in structure, shape or size [22].

Separation of molecules in the feed, having different chemical potentials like pressure or concentration, is achieved by membrane processes [23].

All membrane separations rely on a driving force across the membrane to induce the flow or flux and a separation factor which prevents some materials crossing. Pressure is the most common driving force in that case low-pressure *permeate* stream becomes enriched by rapidly diffusing components while the slower components are concentrated in the *retentate* stream [24, 25]. Either permeate or retentate could be the product.

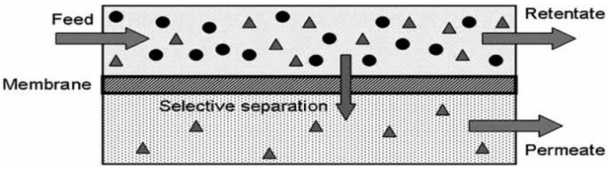


Figure 2.1: Gas transport through dense membrane

Two main characteristics, used for comparison of membrane performance are selectivity and the flow passing through the membrane. The latter, often defined as permeation rate (P), is denoted as the amount of the gas flowing through the membrane per unit area and time.

$$P = \frac{J_i l}{\Delta P_i}$$

Where J_i is the flux of permeating gas *i*, l is the thickness of the particular membrane and ΔP_i is the effective partial pressure difference of species *i* across membrane meaning transmembrane pressure difference. The permeabilities are commonly defined as in the unit of Barrer:

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

The selectivity (α) is the indication of separation ability of a membrane [14]. Ideal selectivity is the ratio of permeabilities of two single gases [24]. It depends on the experimental conditions, such as pressure differences of the applied gases [25].

$$\alpha_{i/y} = \frac{P_i}{P_y}$$

Membrane selectivity towards binary gas mixtures is given as:

$$\propto_{i/y} = \frac{y_i / y_y}{x_i / x_y}$$

where y_i and y_y represents the concentration of components *i* and *y* in the permeate side and x_i and x_y represents the concentration of the components in the feed side. These concentrations are usually given as mole fractions.

2.1.1 Polymeric Membranes:

The membranes currently used in most commercial applications are *solution-diffusion membranes.* These membranes are so named because transport occurs when gas molecules dissolve into the membrane and then diffuse across it.

$$P = S \times D$$

P, S and *D* represent permeability, solubility and diffusivity respectively. Permeability of a membrane depends upon: thermodynamic term, solubility which characterizes sorbed gas molecules under equilibrium conditions and kinetic term, diffusivity which characterizes the mobility of gases that transport through the membrane [26]. Today all of the commercial solution-diffusion membranes are produced from polymeric materials; so, these types of membranes require most of the attention [25].

Permeation coefficient of a polymer is a temperature dependent factor. It is typically modeled by Arrhenius relation for temperature ranges where a thermal transition does not occur:

$$P = P_o \times exp\left(\frac{-E_a}{R \times T}\right)$$

On the same basis both diffusivity and solubility, which is a scale of penetrants condensability, of a polymer can be defined as:

$$D = D_o \times exp\left(\frac{-E_d}{R \times T}\right)$$

$$S = S_o \times exp\left(\frac{-H_s}{R \times T}\right)$$

where $P_{0,}$ $D_{0\,,}$ S_0 [Barrer] are the pre-exponential factors, R [8.314×10−3 kJ/mol K] is the universal gas constant. T [K] is the absolute temperature and $E_{a,}$, E_d are the activation energies for permeation and diffusion respectively. H_s [kJ/mol] is the heat of sorption.

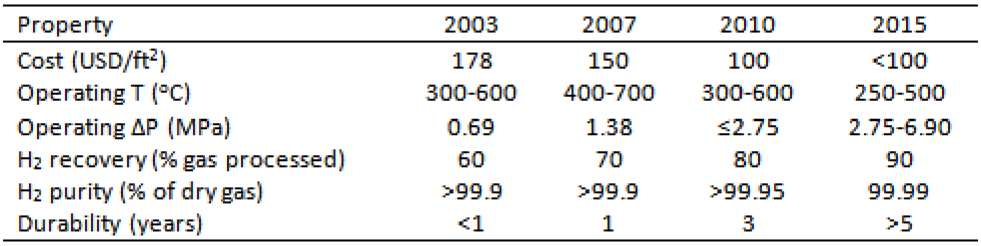
Polymer free volume amount and its distribution are the main criteria in transport of gases. When a polymer is at temperatures above its glass transition temperature under conditions of use, this polymer is in its rubbery state. Rubbery polymers have relatively higher free volume due to mobile polymer chains; therefore rubbery polymers offer high permeabilities. But the selectivity of these polymers depends on the condensability difference of the gas species. When the polymer structure is altered by heat fluctuations, it propels sorption of gas molecules into free volume [24, 26].

On the other hand, when a polymer is at temperatures below its Tg, it is in glassy state. In this case the free volume decreases and polymer backbone has restricted co-operative movements. Due to the more restricted segmental motions, molecular interactions and molecule-chain affinities are involved in glassy polymers, these materials offer enhanced “mobility selectivity” as compared to rubbery polymers. Glassy polymers which are more common in industrial applications, offer higher gas selectivity and they have good mechanical properties [24, 28].

2.2 Hydrogen Carbon Dioxide Separation by Polymeric Membranes

Membrane gas separation has many benefits over conventional process for H_2/CO_2 separation either as a stand-alone process or integrated process with water gas shift reactors. It offers low investment cost, operating at high temperatures and pressures, lowers the energy cost of the process and high pressure retentate CO_2 will be transport and stored without compression.

Table 2.1: Performance targets for H_2 separation membranes [30]



Property	2003	2007	2010	2015
Cost (USD/ft^2)	178	150	100	<100
Operating T (°C)	300-600	400-700	300-600	250-500
Operating ΔP (MPa)	0.69	1.38	≤2.75	2.75-6.90
H_2 recovery (% gas processed)	60	70	80	90
H_2 purity (% of dry gas)	>99.9	>99.9	>99.95	99.99
Durability (years)	<1	1	3	>5

Table 2.1 gives the target property values for H_2 separation membranes tabulated by U.S. Department of Energy. To achieve the desired properties, lower material cost, power demand, production costs and improved hydrogen flux and membrane durability should be obtained [30].

Hydrogen separation membrane materials can be classified as metallic (metals or metal alloys), carbon, organic polymers and inorganics (e.g. zeolite, silicates, etc.). Each class of membranes can provide high performance but have shortcomings in economy or fabrication methods.

Polymers are the cheapest and easily processed material for membrane fabrication. They have great flexibility in their composition and modification is much easier which make them a better choice [21].

In processes designed for hydrogen selective separation by dense, nonporous polymeric membranes have a hydrogen concentrated product stream, the greater amounts of remaining gases usually left in the retentate. Among various gases (CO_2, CH_4 CO, O_2), which are commonly found as impurities in process, require hydrogen separation. Low critical temperature (-240^{o}C) of hydrogen is an indication of lower solubility of this gas. Low solubility combined with small kinetic diameter (0.289 µm) brings demand for diffusivity selective membranes for this application. Therefore, the current hydrogen selective membranes are fabricated in the aim of increasing the diffusivity of hydrogen [21].

Table 2.2: Gas permeabilities of some of the commercial polymeric membranes at 30°C [32]

Polymers	Permeability (Barrer)		H_2/CO_2 Selectivity
	H_2	CO_2	
Ethyl Cellulose	87	26.5	3.28
Polyetherimide	7.8	1.3	5.91
Polyphenyleneoxide	113	75.8	1.49
Polysulfone	14	5.6	2.50
Polymethylpentene	125	84.6	1.48
Polyimide (Matrimid)	28.1	10.7	2.63

Glassy polymers are the most frequently used materials for fabrication for hydrogen selective membrane operations [29, 31]. Table 2.2 gives performance of some of membranes which may be important in H_2/CO_2 separation [32].

Largest selection of polymers for H_2/CO_2 separation was studied by Orme and co-workers [32]. They tried to find a suitable material which can block the CO_2 transport and offers high hydrogen fluxes. Among many polymers polysulfone, polystyrene, poly (methyl methacrylate) and poly (vinylidene fluoride) gave the best separation performance at 30°C. Selectivities of the selected membranes are 2.0, 2.3, 4.0, 2.0 respectively. They concluded that polystyrene is the best choice. It has the best combination for both high selectivity and permeabilities.

Xu et al. [33] examined the performance of fluorine containing poly(arylene ether)s with large and bulky diphenylfluorene moieties (FBP/6FPT and FBP/6FPPr). The selectivities for H_2/CO_2 were not so high; 1.67 for FBP/6FPT membrane and 1.54 for FBP/6FPPr membrane. But the remarkable point in the study is the high diffusivity selectivity almost 100 for hydrogen and carbon dioxide gas pair. Low overall selectivity is a result of poor solubility selectivity.

Polyimide (Matrimid) is one of the most studied polymers for hydrogen separation application. This polymer is chosen because when membranes are produced, they offer high permeability and selectivity, solvent resistance and thermal stability [34]. Smaihi et al. [35] prepared hydrogen selective polyimide membranes. Permeabilities of dense membranes were 1.14 and 3.0 Barrer for CO_2 and H_2 respectively at 35°C. To improve the performance of the neat membranes they have synthesized hybrid imide-siloxane copolymers. Membranes prepared from this copolymer showed a better performance in gas separation, H_2/CO_2 selectivity increased from 2.63 to 3.5 at 35°C.

Hosseini et al. [36] tried to demonstrate the performance of polyimide polymer as a gas separation membrane. Permeability coefficients for hydrogen and carbon dioxide were 27.16 and 7.00 Barrer at 35°C for dense polymeric membrane. The selectivity was almost 4.0.

In a study of our group Şen et al. [37] used polycarbonate membrane for gas separation. Dense polymeric membranes permeabilities for H_2 and CO_2 were 15.3, 8.80 Barrer respectively. But the resultant selectivity was low.

2.3 Polybenzimidazole Gas Separation Membranes

For carbon sequestration and capture at high temperatures with low energy by membranes has become an important issue for obtaining hydrogen.

Current processes used for CO_2 sequestration require cooling of the gases to ambient temperatures [42]. The benefit of using membranes could significantly change the economy of the process. This will be done by using membranes which are stable both thermally and mechanically at high temperatures and pressures.

Aliphatic polybenzimidazole was first invented by Brinker and Robeson. Two years later, Vogel and Marvel synthesized aromatic polybenzimidazole. After taking attention from both academia and industry because of its high thermal and mechanical resistances, various polybenzimidazoles have been invented. But only a few of synthesized polymers showed desired properties. Table 2.3 summarizes the structures and thermal properties of them [38].

Table 2.3: Structural and thermal properties of PBI [38]

Tetraamine	Acid	Melting Point (^oC)	Weight Loss in N_2 (%)*	Weight loss in air (%)*
Bisphenyl	3,4-Diaminobenzoic Terephthalic	>600	0.4	
Benzene	Terephthalic	>600	0	
Biphenyl	Isophthalic	>600	0.4	5.2
Benzene	Isophthalic	>600	0.3	
Diphenylether	Isophthalic	>400		
Biphenyl	Phthalic	>500	0.4	7.0
Biphenyl	4,4’-Oxydibenzoic	>400		
Biphenyl	Biphenyl-4,4’ diacid	>600	0.8	
Biphenyl	Biphenyl-2,2’ diacid	>430	8.0	

*: Weight loss after 1 hour at 500^oC, after heating 1 hour at 400 and 450^oC

Polybenzimidazole synthesized from monomers terephthalic acid and bisphenyltetraamine was found to be worth to investigate. This polymer is called Poly (2,2’-(m-phenylene)-5,5’ bibenzimidazole) (PBI) and its structure is given in Figure 2.2. This heterocyclic PBI having glass transition temperature of 400-435^oC, possesses good thermal, mechanical and chemical stabilities (up to 550^oC) [39, 63]. Hence, PBI-based materials are suitable for extreme chemical and thermal conditions. Also, PBI processability level makes it a better choice when compared to other polymers in the Polybenzimidazole family.

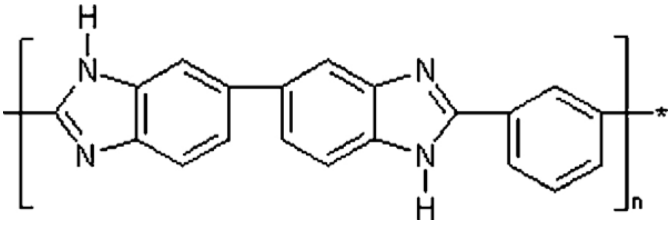


Figure 2.2: Poly(2,2-(m-phenylene)-5,5-bibenzimidazole) (PBI) structure

PBI has become the first commercial polybenzimidazole polymer, produced by Hoechst Celanese using the trade name Celazole® [38]. Since then operability of PBI at harsh conditions provided usage of this material in fire controlling for asbestos replacement, ultrafiltration, reverse osmosis, hydrogen purification, fuel cells [40], electrolysis and electrochemical sensors [41]. PBI as a membrane material has received attention in the late 1960s.

To obtain a dense polymeric membrane solubility of the polymer is an essential issue. One of the drawbacks of PBI polymer is its poor solubility. It is soluble in common organic solvents only at high temperatures [38]. Klaehn et al. [43] studied on modifying PBI by N-substitution the imidazole nitrogens. Two types of modification were applied on polymer; silane and organic compounds substitution. Molecular weights of new polymers were higher than unsubstitued PBI. Using small molecule organic compounds molecular weight increased drastically. It was contributed to the crosslinking. Obtained polymers were soluable in tetrahyrofuran. But they couldn't obtain desirable film formation properties, since films were fractured.

PBI demonstrates a selective separation of H_2 from other gases present in reforming mixture. But dense structure of the polymeric material prevents high gas permeabilities of gases. To overcome the structural drawback of this polymer, coming from intermolecular hydrogen bonding and chain rigidity attempts have been done [41]. These include production of composite membranes or carbon membranes, structural modifications of membranes, and preparing supported membranes [43-49].

Han et al. [41] attempted to develop PBI membrane with higher gas permeabilities. Different synthesized precursor polymers are used to produce thermally rearranged (TR) PBI polymers. Controlled synthesis of PBI prevented the high packing density in polymer matrix. Evaluation of gas permeation performance of the prepared membranes were done using pure gas feed containing CO_2, H_2, O_2, N_2 and CH_4. The permeability order of gases was $H_2>CO_2>O_2>N_2>CH_4$. TR-PBI membranes possessed increase in gas permeabilities when compared to the precursor polymers. Furthermore, at elevated operating temperatures small gas molecules, H_2 and O_2, permeabilities increased but same trend couldn't be observed for the other gases. H_2 permeability didn't show a remarkable increase in the temperature range tested, but CO_2 solubility and therefore its permeability decreased. These membranes showed advantageous performance especially for H_2 and CO_2 separation at 120^oC.

In another study done by Pesiri and co-workers [44, 45] PBI meniscus membrane, which has a concave shape, suitable for hydrogen and carbon dioxide separation at high temperature were produced. PBI meniscus membranes span a tiny hole in the middle of the thin film. They mentioned that membranes produced from PBI polymer are poor room temperature separation membranes. Their initial focus was testing produced membranes close to temperatures in the industrial scale operations. The operating temperatures of the experiments were extended up to 340^oC. After 100^oC significant increase in permeance for both gases were observed. Both selectivity and flux have showed a positive trend by increasing temperature for single gas experiments. During mixed gas experiment hydrogen permeance values declined after 250^oC. The selectivity increased up to 20 for H_2/CO_2 until 270^oC but at 320^oC it decreases to 3.0. Carbon dioxide offsets the permeance of hydrogen.

To ameliorate the performance of PBI membranes Kumbharkar et al. [46] investigated the gas permeabilities of H_2, CO_2, O_2, N_2 and CH_4 through modified PBI membranes. The aim of the study is to draw the advantage of PBI structural properties by modifying the structure. Two different PBIs one based on isophthalic acid (PBI-I) and other one based on 5-tert-butyl isophthalic acid (PBI-BuI) were used for substitution. Different N-substitutions were employed by n-butyl, methyl, *4*-tert-butylbenzyl and methylene trimethylsilyl groups on PBIs which has different acid moieties. PBI-BuI showed higher permeabilites but lower selectivities than PBI-I after substituted by a particular group. Changing the substituent groups changed the diffusivities in an extended level compared to solubilities. Methyl, which is the smallest group, substitution exhibited the highest selectivity but lowest permeabilities among other substituent groups. Tert-butlybenzyl group substituted PBIs showed an opposite trend. By substitution, the gas permeabilities of different gases enhanced 1.2-129 times.

Same group studied the effect of casting solvent on the same substituted polymers [47]. They claimed that performance of a membrane varies as a function of casting solvent. Viscosities of membrane preparation solutions were measured. Addition of substitution groups lowered the viscosity ascribed to the loosening intermolecular hydrogen bonding. Elimination of intermolecular bonding provided by substitution improved the solubility of PBIs. Prepared polymers were soluble in chlorinated solvents besides DMAc or NMP. To assess the effect of substitution, gas permeation tests was done using helium and argon gases. In general an increase in permeabilities was observed by substitution. The extent of the change depends on the structure of different prepared polymers [47].

Berchtold and co-workers [48] focused on producing PBI membranes which are durable at industrial operating conditions. Composite membranes were prepared by covering the surface of porous stainless steel support by PBI layer. A zirconia layer presents on the stainless steel support as an intermediate layer between steel and polymer. Obtained ideal selectivities for H_2/CO_2 and H_2/N_2 gases were 43 and 233 respectively at 250^oC and 3.5 atm. By increasing the temperature from 150 to 250^oC, selectivities of composite membranes decreased from 58 to 40. To simulate the realistic conditions a gas mixture containing CO_2: 41%, H_2: 55%, CO: 1%, CH_4: 1%, H_2S: 1% and N_2 1% at 250^oC and 3.5 atm were used. Similar selectivity results for H_2/CO_2 gas pair were obtained. Presence of corrosive or plasticizer gases like H_2S and CO_2 didn't have an effect on the composite membranes. The stabilities of membranes were demonstrated by long term durability tests at 250^oC for 330 days. As a result under simulated synthesis gas conditions membranes performance didn't change drastically.

Alternatively, Hosseini et al. [49] used blends of PBI and polyimides (Matrimid, Torlon and P84) for carbon membrane formation. The fundamental reason for this idea is to improve the resistance of brittle PBI membranes. The origin of the idea is based on the good compatibility and miscibility of PBI with some other polymers [50-51]. 50/50 wt.% blend precursors showed almost same performance as individual polymers. On the other hand, carbon membranes prepared from these blend precursors exhibited much higher permeabilities. Selectivities also showed an increase to some extent. PBI/Matrimid carbon membrane possessed the higher selectivity for most of the gas pairs, which is more evident for H_2/CO_2, the selectivity changed from 6.05 to 8.85 after carbonization. The results revealed that the blend precursor structure has an important contribution for the final properties of carbon membranes. Also effect of blend polymers compositions was studied. The membranes prepared by using higher amount of PBI, which has less non-carbon parts, showed much better performance. This result supports fine pore formation during carbonization. The selectivity for H_2/CO_2 improved from 6.84 to 9.2 for PBI/Matrimid membrane as PBI content increased from 25 to 75 wt.%.

Jorgersen et al. [52] prepared crosslinked PBI membranes supported on stainless steel substrate. Weight percent of the crosslinker α,α'dibromo-p-xylene was arranged as 10 wt.%. By rising temperature favorable permeabilities for N_2, CO_2, CH_4 and H_2 were obtained. But selectivities affected adversely except for H_2 and CO_2 gas pair. Selectivity almost stayed same for this pair. They concluded that this membrane may be a proper choice at elevated temperatures for H_2/CO_2 separation when the economics of the system is considered.

To take benefit from structural advantages of PBI and to overcome the major structural drawbacks some modifications have been done as stated in above researches. Another way of improving the performance of polymeric materials is producing inorganic incorporated polymeric membranes called Mixed Matrix Membranes.

2.4 Mixed Matrix Membranes

In 1991, Robeson plotted the selectivity versus permeability data for many different gas pairs tested using various polymers and found that they lay on or below a specific line which is called “Upper Bound Tradeoff Line” [53].

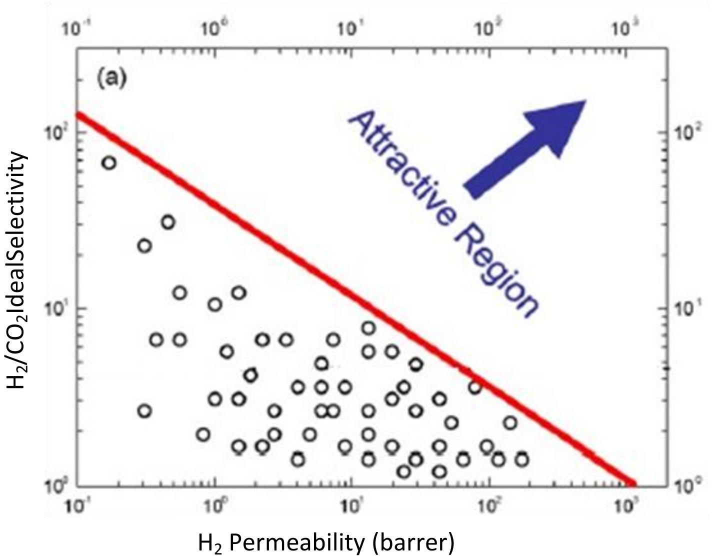


Figure 2.3: Upper bound line for H_2 selective membranes

Figure 2.3 depicts the tradeoff between permeability and selectivity for hydrogen and carbon dioxide gas pair. The relationship between permeability and selectivity was described by Robeson as shown in below equation:

$$\alpha_{A/B} = \frac{\beta_{A/B}}{P_A^{\gamma_{A/B}}}$$

where $\beta_{A/B}$ and $\gamma_{A/B}$ are parameters which were reported by Robeson for some gas pairs. On the other hand, Freeman et al. [105] introduced a theory to explain the upper bound line. According to this theory $\gamma_{A/B}$ is related to the penetrant kinetic diameters and $\beta_{A/B}$ related to condensability of gases. It was stated that attractive region could not be reached by changing chemical structure of the polymer, since related parameters are only dependent on the gases.

Attractive region for industrial applications is beyond this upper bound line as shown in Figure 2.3. A substantial effort has been made to overcome this limit. Molecular sieve membranes like carbon sieve, zeolite membranes or metal organic frameworks show performance above the upper bound line [12]. But these materials are expensive to produce and they are very brittle. Furthermore, obtaining modules with high surface area using these materials is very difficult because of their fragile nature [12, 53, 54].

Mixed matrix membranes (MMMs) became a potential approach for gas separation [65-66]. They are produced in the purpose of combining the good gas separation properties of inorganic materials and easy processability of polymeric materials to obtain more efficient membranes [55, 56]. The degree of mobility of the polymers chains often limits the size sieving abilities and most of the time at high temperatures they are not stable. On the other hand, inorganic materials offer high temperature resistance. Thus, inorganic materials having the unique structural and separation properties are dispersed in polymer matrix to obtain better performance than conventional polymeric membranes. As a result, the benefit of dispersed filler particles includes acting as a block for undesired gases transport, increasing permeabilities and disturbing the structure [57, 91].

Either porous or nonporous inorganic materials can be used for MMMs preparation. Porous type of fillers discriminate the molecules according to their size and shape. Hence, they have high selectivities and permeabilities above the tradeoff line. Adding porous fillers into the polymer matrix increases the overall selectivity of the membranes relative to neat membrane [58-60]. On the other hand, nonporous fillers may enhance the separation characteristics of MMMs via increasing free volume by changing distance between polymer chains. Increased tortuosity by increasing amount of filler can reduce the diffusion of large molecules [63, 64]. In contrast, nano-scale particles may disturb the chain packing of the polymer matrix and increase free volume which may result in increased diffusion of gases [61].

Glassy or rubbery polymers can be used as polymer matrix. Rubbery polymers can provide good adhesion between zeolite and polymer. But, their gas separation performances are still below compared to glassy polymers which make them less attractive candidates compared to glassy polymers.

Glassy polymers possess performances close to the upper bound line and they have higher mechanical stabilities. Thus, more researchers focused on studies employing glassy polymers as matrix [61, 67-69].

Zornoza et al. [62] prepared mixed matrix membranes by employing hollow microporous silicalite-1 spheres (HZSs). The advantage of addition of this type of filler was demonstrated by using polysulfone and polyimide. The results were promising for H_2/CH_4, CO_2/N_2, and O_2/N_2 gas mixtures at 8 wt.% loading for both membranes.

Zeolites are able to discriminate molecules according to their size precisely. Zeolite/polymer MMMs are candidates to appeal to the problems encountering with both polymers and zeolite membranes [104]. For suitable combination not only the polymer and filler type but also, the size and loading of the filler and membrane preparation parameters have major influence on the separation properties [61,105].

In our research group many studies for improving gas separation of polymeric membranes by producing mixed matrix membranes were investigated [37, 71-75].

Şen et al. [37] used polycarbonate (PC) as polymer matrix, Zeolite 4A as filler and *p*-nitroaniline (pNA) as low-molecular weight additive. Neat PC, PC/pNA, PC/zeolite 4A and PC/pNA/zeolite 4A mixed matrix membranes were produced. The additive concentration changed from 1 to 5 wt.% for pNA and filler concentration from 5 to 30 wt.% for Zeolite 4A. H_2, CH_4, O_2, CO_2, N_2 gases were tested for gas permeation measurements to examine the effect of additives. The gas permeation performance of the neat PC membranes enhanced remarkably by incorporation of additives. Highest ideal selectivities were obtained for PC/pNA/zeolite 4A mixed matrix membranes. CO_2/CH_4 selectivity increased from 23.6 to 51.8 and for H_2/CH_4 increased from 40.9 to 121.3.

In a study done by our group Karatay et al. [71] prepared binary and ternary mixed matrix membranes by using SAPO-34 as filler, 2-hydroxy 5-methyl aniline (HMA) as compatibilizer and polyethersulfone (PES) as polymer matrix. Incorporation of additive to the structure may enhance the performance of MMMs by increasing the link between filler and polymer [68-70]. The lack of contact between polymer and zeolite causes dramatic decline in the performance of membranes by introducing voids for passage of molecules without any size discrimination. Test runs done by utilizing 20 wt.% SAPO-34 loaded membranes resulted in increased permeabilities. The selectivities increased for specific gas pairs, the increase for H_2/CO_2 gas pair changed almost 2 fold, but permeabilities were declined. Among all tested membranes ternary ones gave the best results.

In another study of our group Cakal et al. [74] produced four different types of membranes to see the influence of additives on CO_2/CH_4 separation. For this purpose PES/SAPO-34, PES/HMA and PES/SAPO-34/HMA membranes were prepared. Also neat PES membranes were prepared to see the influence of additives more clearly. Gas mixtures containing 5 to 70 % by volume CO_2 was used as feed. Highest permeability was obtained for PES/SAPO-34 membranes while highest selectivities were obtained for PES/SAPO-34/HMA membrane containing 4 wt.% HMA. The results showed that regardless of the feed composition, same gas separation selectivities for both single and mixed gas measurements can be obtained.

Furthermore, Keser et al. [75] was focused on producing mixed matrix membranes using PES, synthesized Zeolitic Imidazolate Framewok-8 (ZIF-8) and HMA. In order to demonstrate the zeolite loading influence, concentration was changed between 10 to 30 wt.%. Ternary mixed matrix membranes containing both filler and additive were fabricated. Gas separation performances of the prepared membranes were evaluated by using H_2, CO_2 and CH_4. To elucidate the effect of pressure on these membranes, feed pressure was changed from 3-12 bar. By zeolite addition the permeabilities for all test gases were improved with a slight decrease in ideal selectivities. Incorporation of HMA ideal selectivities increased along with decrease in permeabilities. Selectivities improved from 61.8 to 103.7 for H_2/CH_4 gas pair. On the other hand, permeability decay for H_2 from 26.3 to 13.7 Barrer was evident. Favorable increase was observed in gas separation performance for all types of membranes. It was concluded that it will be proper to work at high feed pressures by using this type of ternary membrane.

Zhang et al. [68] prepared mixed matrix membranes using Polyimide (Matrimid) and mesaporous ZSM-5 nanoparticles. Pure gas tests were employed by H_2, CO_2, CH_4, O_2, and N_2 gases. Increased loading from 0 to 20 wt.% increased permeabilities of O_2, CO_2, H_2. Size sieving ability of the mesaporous ZSM-5 was related to the polymer chain penetration into the zeolite during membrane preparation. In the scope of the same study membranes containing 10 % MCM-48 was also tested. Selectivity improved for H_2/CO_2 gas pair from 2.40 to 2.57 for 20 % ZSM-5 loading and from 2.40 to 2.47 for 10 % MCM-48 loading.

In a study conducted by Josephine and co-workers [69] ZIF-8 nanoparticles filled mixed matrix membranes were prepared using polyimide polymer matrix. Membranes containing higher up to 60 wt.% ZIF-8 nanoparticles were tested for gas permeations of several gases including H_2, CO_2, O_2, N_2, CH_4, C_3H_8. Permeabilities of all gases were altered up to 40 % loading. Further loading of nanoparticles resulted in unfavorable permeabilities. This result was contributed to the more tortuous pathway of mixed matrix membrane for penetrants. Also, it was mentioned that after certain limit of loading, sieving effect of zeolite nanoparticles becomes more dominant instead of polymer free-volume transport. Ideal selectivity for H_2/CO_2 increased from 2.96 to 4.43 as loading increased to 60%.

Huang et al. [70] employed zeolite 4A particles for PES based MMMs. Well-distributed nano-scale zeolite particles provided increased selectivities for He/N_2, H_2/N_2, He/CO_2, and H_2/CO_2 gas pairs when compared to neat PES membranes. Almost 150 % improvement was observed in selectivities for certain gas pairs. The increase was 135 % for H_2/CO_2 selectivity.

To enhance the performance of PBI membranes Choi et al. [61] prepared composite PBI membranes with Arnhernt-3 (AHM-3). This material has a layered structure. The main reason of this choice was permeable layers of the material which provide access from all directions for especially small molecules. The effect of incorporation was tested by gas permeation experiments of hydrogen and carbon dioxide. Proton exchanged (PAHM) and swollen (SAHM) AHM-3 was added to the polymer continuous phase. Permeabilities of gases were declined by increasing load of filler. Membranes prepared by addition of 3 % SMAH and 14 % PAMH almost showed same performance. This result was related to the increasing tortuosity coming from different preparation procedure of these membranes. Ideal selectivity of H_2/CO_2 gas pair was changed from 15 to almost 30 at 35°C. In the scope of the same study to observe the effect of different material incorporation, mixed matrix membranes with plate-like MCM-22 were prepared. Increasing content of MCM-22 altered the permeabilities but ideal selectivities deteriorated. This was attributed to the micro voids formed around aggregated MCM-22 particles. Subsequently, no significant improvement was observed compared to dense PBI membranes [61].

2.5 Effect of Annealing Conditions

The structure of a membrane is an important criterion in determining the right application area of use. The main aim in membrane fabrication is achieving the combination of high selectivity and high gas permeability for a particular application. Hence to make a membrane having desired properties studying formation procedures is crucial [76, 77].

Annealing is a heat-treatment which is applied on membranes to remove the residual solvent trapped within the membrane and to erase the thermal history. Type and conditions of the annealing method have different influences on membranes depending on the structure.

Annealing at different temperatures can change the intrinsic properties of membranes. Kusworo et al. [76] investigated the effect of this phenomenon by preparing polyethersulfone/polyimide blend and annealed them at temperatures both above and below the glass transition temperature of the blend. The permeabilities for O_2 and N_2 were declined by increasing annealing temperature. Initially, annealing at 150°C and 240°C were employed. But the selectivities of obtained membrane were far lower than the unannealed membrane. Increasing the temperature up to 280°C improved the selectivities almost by factor 5. They interpreted that annealing above T_g of the polymer was an effective method to erase the residual solvent imprints.

Macchione et al [79] studied the effect of remaining solvent on Hyflon® AD 60X membranes. They have prepared dense gas separation membranes and the membranes were heat treated under vacuum by heating from 70°C to 200°C slowly. They have tested both unannealed membranes and high temperature annealed membranes using He, O_2, CO_2, H_2 and CH_4. It was concluded that the size sieving properties of membranes were improved after annealing due to reduced chain mobility. The diffusion coefficient of helium remained nearly constant but the diffusion coefficient of CH_4 reduced by almost one order of magnitude.

Fu et al. [80] surveyed the influence of residual solvent on the dense polyimide membranes at both 25°C and 150°C under vacuum for 0.5 to 9 days. Low temperature was not enough to expel residual solvent. They mentioned that at 150°C the mobility of the polymer chains are higher hence, the diffusion of solvent is fast. Increasing residual solvent amount, increased the permeabilities of both N_2 and O_2, meaning after a critical value remaining solvent plasticizes membranes.

To demonstrate the time and temperature dependency of annealing Joly et al. [81] investigated the effect of solvent remaining in 6FDA–*m*PDA polyimide membranes. The prepared dense films were heat treated at 200°C for different period of times. The thermal treatment applied at longer periods provided lower diffusion coefficients but higher permeability and solubility coefficients for CO_2 and N_2 gases. At longer periods the imprint of solvent inside the membrane is eliminated. Also, in the scope of the study they studied different types of solvents for membrane fabrication. They concluded that high molar volume solvents leave imprints within the structure.

Annealing time effect on permeation of carbon dioxide, nitrogen and oxygen gases through co-extruded linear low-density polyethylene was investigated by Lopez and co-workers [82]. The time and the temperature of the process changed from 0 to 24 hours and 0 to 90°C respectively. Permeabilities increased with increasing temperature. The permeation results indicate that nitrogen is not influenced by the time compared to other gases. As the time of annealing changed from 0 to 24 hour, the diffusivity of all gases declined gradually. But the permeabilities showed an opposite trend. They related this to the melting of very small crystalline parts on the polymer chains according to the DSC diagrams.

In our group Hacarlıoğlu et al. [83] reported the effect of annealing time on dense polycarbonate membranes. Annealing was employed at 50°C for 8, 24, 72, 154 hours. Denser structures were obtained as a result of annealing. After 24 hours the permeabilities were declined, but selectivities increased. On the other hand, permeabilities of various gases stayed almost constant between 72 and 154 hour annealing. They concluded that 72 hour annealing was enough to destroy solvent imprints within the structure of the membrane.

Kruczek et al. [84] studied an alternative annealing method by using sulfonated polyphenylene oxide. Additional heat treatment after solvent evaporation is not a proper method for the complete removal of entrapped residual solvent in the prepared membranes because of the decomposition of the sulfonic groups at high temperatures. Therefore, they decided to remove the residual solvent by long-term permeation of CO_2 gas through the membrane. The permeation rate of CO_2 increased in the first 3 days of the experiment, but no change in permeation values of CO_2 were observed between 3-63 days. They concluded that there was no possibility for solvent presence in the membrane structure after 63 days.

Hibshman et al. [85] investigated the effect of annealing on gas permeation performance of partially hydrolyzed polyimide membranes. Annealing at 400°C and then decreasing the temperature by quenching caused cross-inking within the structure. This was evident with the results of TGA-MS, FTIR-ATR. Membranes were characterized by single gas permeabilities for He, O_2, N_2, CH_4, CO_2 at 35°C. The permeabilities increased almost 2 to 3 fold. Results were attributed to altered local molecular motions on the polymer chain. Diffusivity dominant permeation was observed. But selectivities declined.

To determine the effect of annealing temperature on membrane performance, Koros and co-workers [86] examined synthesized fluorinated, 6FDA based polyamide–imide for the separation of CH_4 from streams containing plasticizers like CO_2 and H_2S by dense membranes annealed at various temperatures. 200°C was found to be the best temperature for annealing.

2.6 Effect of Operating Temperature:

Many attempts have been done to increase the performance of a membrane showing high permeability and selectivity for higher product purity. On the other hand, it is important to obtain membranes not only showing high but stable performances at harsh industrial operating conditions.

In literature most of the studies related to gas separation membranes were done at low operating temperatures. Even Robeson trade-off line was plotted using measurements carried out at temperatures between 25°C-35°C [53]. The effect of temperature on upper bound line has been investigated recently [115]. If the aim is obtaining high performance membranes especially for high temperature applications, to fully explore the performance of prepared membranes, it is crucial to study at higher temperatures.

Mobility of polymer packed structure and intersegments are temperature dependent [80]. At elevated temperatures, the diffusivity of molecules and segmental motions increase, resulting in higher transportation rates. Specific gas molecules which possess higher activation energies are more influenced by the temperature [81, 83].

Merkel et al. [88] investigated the permeability of syngas feed containing H_2, H_2S, CO and CO_2 at temperatures changing from room temperature up to 240^{o}C. The simulated feed was tested using solubility selective rubbery poly(dimethylsiloxane) (PDMS) and glassy poly(1-trimethylsilyl-1-propyne) (PTMSP) polymers. At room temperature both membranes showed higher permeabilities for H_2S and CO_2. At elevated temperatures they became hydrogen selective. At higher temperatures permeability of all gases except hydrogen decreased for PTMSP polymer indicating negative activation energies. But for PDMS all gases gave positive activation energies. The calculated activation energies were highest for hydrogen and decreased according to the solubilities of gases.

Mixed matrix membranes were prepared using polysulfone acrylate-zeolite 3A and studied as a function of temperature for H_2/CO_2 separation. The operating temperature changed from 25^{o}C to 55^{o}C. Diffusivity of both gases increased with rising temperature as a result of enhanced flexibility within polymer chains. But CO_2 permeability increase was more significant compared the H_2 selectivity which in turn results in decrease in selectivity with temperature [90].

In our group Oral et al. [74] used four different membranes to investigate the effect of annealing time and temperature on performance of membranes. These membranes include neat PES and PES/SAPO-34, PES/SAPO-34/ HMA and PES/HMA mixed matrix membranes. Neat PES membrane showed stable permeation results. But same trend couldn't be observed for other types of membranes. Therefore, post annealing was applied at 120^{o}C, 0.2 atm and 7-30 days. After post annealing, membranes showed higher and stable gas permeations for all tested gases.

Diaz et al. [91] worked with H_2, N_2, O_2, CO_2, CH_4, C_2H_6 and C_2H_4 gases to explore the performance of poly(1,4-phenylen ether-ether-sulfone) membranes containing ZIF-8 particles as filler. For all tested gases permeabilities increased as a result of improved diffusion. Hydrogen was the only molecule which exhibited endothermic sorption process for both neat and MMMs as a result diffusion dominant permeation was observed for prepared MMMs.

Ostwal et al. [93] studied the transport properties of carbon dioxide and nitrogen with poly(fluoroalkoxyphosphazene) membranes. Increasing temperature from -15^{o}C to 30^{o}C increased the permeability of CO_2 from 142 Barrer to 336 Barrer. Ideal selectivity for CO_2/N_2 changed from 21 to 12 at 3 bar feed pressure. Solubility coefficient of CO_2 deteriorated as temperature increase on the other hand, diffusivity coefficient showed an opposite trend.

Koros and Castello [87] investigated the change in gas permeation performance of three different polycarbonate polymers as a function of temperature. Bisphenol-A polycarbonate, tetramethyl polycarbonate, and tetramethylhexafluoro polycarbonate were tested using CO_2, CH_4, He and N_2 between 35°C- 125°C. Permeabilities of gases were increased via operating temperature rise, but selectivities declined. The loss in CO_2/CH_4 and He/N_2 selectivity were related to the decrease in both solubility and diffusivity selectivities. Membranes prepared by tetramethylhexafluoro polycarbonate gave the best performances.

2.7 Selection of Membranes Preparation Materials

Proper selection of materials for the fabrication of mixed matrix membranes is a crucial factor. Inorganic fillers act as molecular sieves and transport in polymers are related to the selection characteristic of the material. Therefore, both polymer and filler phase has an influence on mixed matrix membranes separation properties [58-60, 91].

In membrane separation applications it is fundamental to choose membranes which show high selectivity and permeability at the same time along with good mechanical and chemical strength, thermal stability and low manufacturing cost.

Since water gas shift reaction occurs at high temperatures and pressures it is beneficial to perform H_2/CO_2 separation at corresponding conditions. When membranes are stable at high temperatures and pressures they may selectively remove hydrogen and carbon dioxide. In this study PBI was chosen as polymer matrix. PBI which can retain its integrity at high temperature is a potentially suitable selection for gas separation purposes.

PBI polymer has some shortcoming related to its intrinsic properties. Its relatively high chain packing density provides a rigid structure which exhibits some drawbacks in gas separation. Highly packed structure of this polymer limits permeability of gases. In order to enhance the gas separation properties many attempts were used including producing mixed matrix membranes as mentioned in Section 2.3.

Suitable filler choice can provide a good interfacial contact with polymer. Contact between polymer and zeolite should be sufficient enough to eliminate gaps between two phases and not block the pores of the zeolite [61, 63]. The molecular sieve filler involved in the study were SAPO-34 and Zeolite 3A. Zeolite 3A is a kind of zeolite having pore size of 0.3 nm which can discriminate hydrogen and carbon dioxide molecules having kinetic diameters of 0.289 and 0.33 nm respectively. Synthesized SAPO-34 was used as second filler. The particle size of this zeolite may provide homogeneous distribution within the membrane [95, 96].

In this study the influence of annealing time and temperature and operating temperature on performance of neat polymeric and mixed matrix membranes are investigated systematically with single gas permeabilities of H_2 and CO_2 gases.

CHAPTER 3

EXPERIMENTAL

3.1 Materials for Membrane Preparation:

Polymer: A commercial polybenzimidazole containing repeating benzimidazole groups supplied from both Celanese (PBI-1) and FumaTech polymer under the tradename of Fumian AP (PBI-2). Fumian AP has average molecular weight (M_n) of 45000 g/mol. The structure of the polymer is shown in Figure 3.1. Membranes MB-1 to MB-5 were prepared by using PBI-1 and the rest of the membranes were prepared by PBI-2.

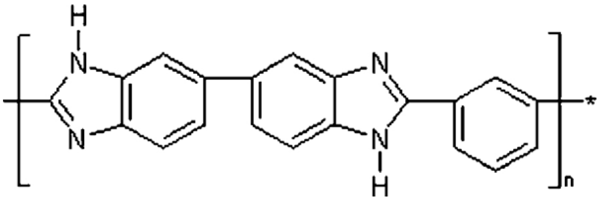


Figure 3.1: Repeating unit of Poly (2,2'-(m-phenylene)-5,5' bibenzimidazole) (PBI)

Solvent: PBI gas separation membrane is usually prepared by solution casting method [44-48]. PBI (Figure 3.1) is a heterocyclic polymer which contains both proton donor (-NH-) and proton acceptor (-N=) sites that can interact with protic and aprotic polar solvents [99]. Organic solvent including N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and mixtures of ethanol and sodium hydroxide (NaOH) can be used for dissolving the polymer [98]. In this study N,N-dimethylacetamide (DMAc) which is a good solvent for PBI was used. It is a common solvent used for preparation of membranes [99]. Analytical grade polar aprotic solvent N,N-Dimethylacetamide (DMAc) purchased from Sigma Aldrich which has a boiling point of 165°C was used as solvent. The formula of linear structure is $CH_3CON(CH_3)_2$.

Inorganic Filler: Commercial Zeolite 3A having a chemical formula of $K_{12}[(AlO_2)_{12}(SiO_2)_{12}]$ was used which was supplied by Sigma Aldrich and sub-micrometer size SAPO-34 (silicoaluminophospate-34) having a molar composition of $1Al_2O_3:1.5P_2O_5:0.3SiO_2:3TEAOH:101H_2O$, synthesized in our laboratory [93], was used as second filler. Zeolite 3A has pore size of 0.3 nm and average particle size of 5 µm which is reported by Sigma Aldrich. SAPO-34 particles have a pore size of 0.38 nm, average particle size of 200 nm measured by Malvern Mastersizer 2000. The particle size distribution of SAPO-34 particles is given in Appendix A.

3.2 Membrane Preparation Methodology

Solvent evaporation method was utilized for preparing thin film membranes. Three kinds of membranes were prepared; neat PBI, PBI/Zeolite 3A and PBI/SAPO-34. Fillers were dried at 250°C for 1 day prior to membrane preparation.

Solubility of PBI polymer in common solvent is a problem for especially commercially supplied polymers [97]. Not complete but >90% solubility in DMAc was reported by FumaTech. There was no specific information about the solubility of PBI-1. Yet during casting solution preparation, for both type of polymer the amount of undissolved polymer after dissolution was measured. The results were similar.

Casting solution preparation:

Casting solution concentration has significant effect on membrane performance [83]. To determine the proper polymer concentration for membrane production, concentration was changed between 2-10 wt.%. This concentration determination study was performed by PBI-1. It was observed that for all concentrations heating at 100°C on a hot plate with stirring for 4 days was not enough. Hence, a new set-up shown in Figure 3.2 was installed under our laboratory conditions.

In the new set-up a flask containing polymer and solvent was placed in a silicon oil bath. This bath was on a hot plate and used for supplying a homogeneous heating. By using this system dissolution was operated at 140°C, which is closer to the boiling point of DMAc, under stirring. The temperature of the system was controlled by both a thermocouple and a thermometer. Continuous nitrogen feed as a sweep gas was send into the flask at very low pressures. The aim of using a sweep gas was to cut the contact of polymer solution surface with the air. Besides to prevent the boiling of solvent a condenser was used. 10±1 °C water was supplied to the condenser by a cryostat which was utilized to recycle the evaporated solvent.

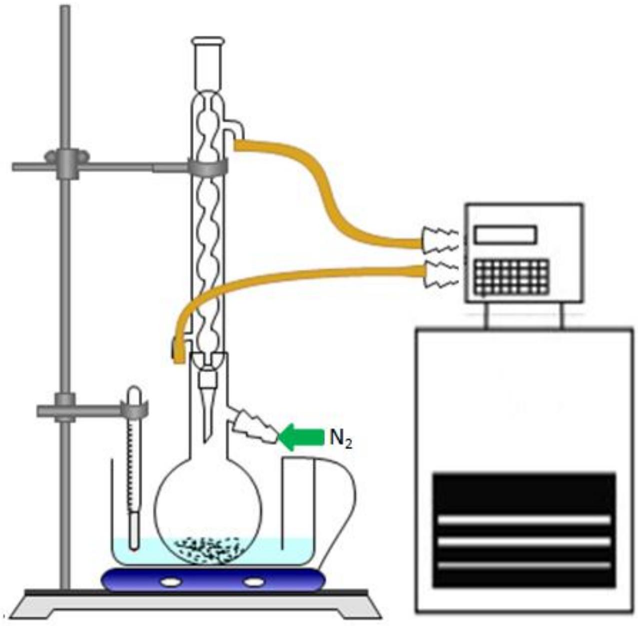


Figure 3.2: Set-up used for casting solution preparation

Initially this system was used for 2 wt.% casting solution. Then, 5 wt.% solution was prepared. The dissolution problem continued at all concentration range studied. Also, the undissolved part of the polymer was difficult to separate. Therefore, higher polymer concentrations were not studied. This advantageous new system provided homogeneous heating of the solution and lowered the dissolution time to 2 days for 2 wt. % casting solution.

The main reason of dissolution problem was using the commercial polymer which has a high molecular weight. Furthermore, it was decided that without changing the structure of the polymer, this problem could not be solved. For this reason, to enhance the solubility, 1 wt. % LiCl was added to the polymer solution. Obtained membranes washed with deionized water and dried at 60°C. Particularly, after drying, membranes lost their flat shape and became twisted. As a result this method was not applied in further studies.

After determining the optimum casting solution concentration, the amounts of components were adjusted by considering the dissolution problem of the polymer. For this purpose 2.2 w/v % percent polymer was added to cold DMAc, and the solution was prepared by dissolving the polymer at 140°C for 48 hours under continuous stirring and nitrogen atmosphere. A simple schematic representation of the process can be seen in Figure 3.3. The amount of solution was weighted before and after dissolution process to make sure no solvent was lost from the condenser. If any loss in solvent was observed, required amount was added and solution was stirred for two more hours. After dissolution, the polymer solution was filtered to remove the undissolved part by using Grade 41 ashless Whatmann filter paper (110 mm diameter). The amount of the undissolved, dry polymer was weighted and found to be about 10% of the initial polymer. Therefore, final composition of casting solution was 2 wt. %.

Neat PBI membrane preparation:

Solution casting method was employed for obtaining thin film membranes. The prepared solution was drop cast on two 6 cm Petri Dishes at atmospheric conditions under fume cupboard.

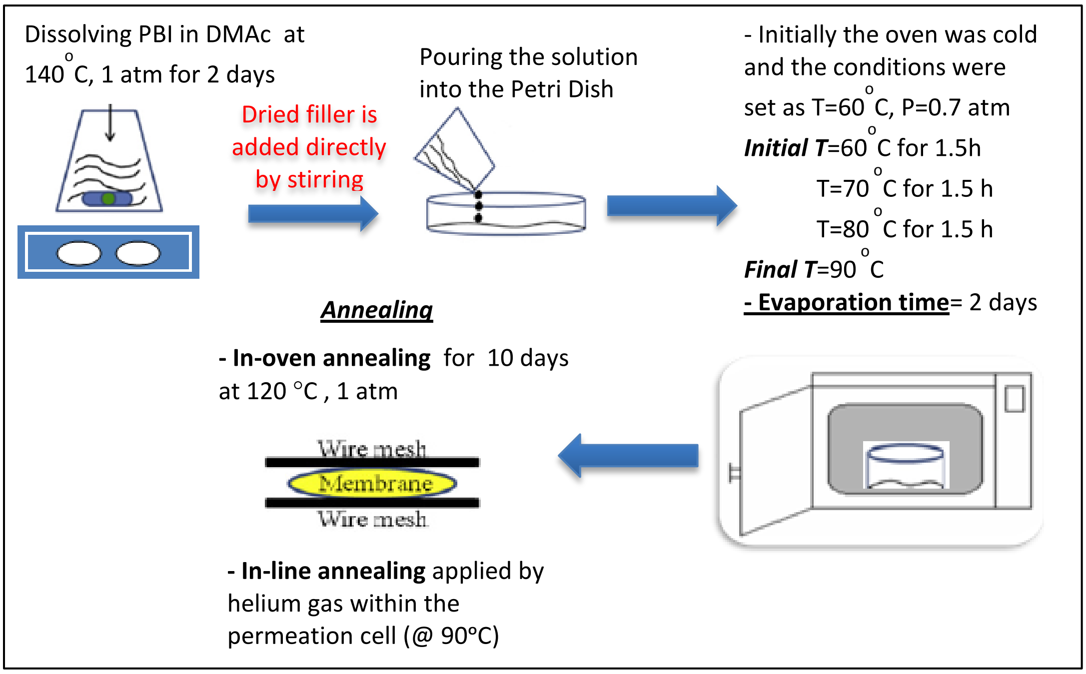


Figure 3.3: Schematic representation of membrane preparation procedure

In the earlier studies Petri Dishes filled with casting solution were located in an oven at 90 °C and 120°C at 0.2 atm vacuum. When the polymer solutions were placed in an oven at 120°C immediate shrinkage of the solution was observed. At 90°C a dense film was obtained but shrinkage problem was continued. Round cut membranes could not been obtained by using these thin films. For this reason, it was decided to start evaporation at lower temperatures and increase the temperature every 1.5 hour period by 10°C intervals at the same time applying 0.7 atm pressure.

Petri Dishes were located in an oven at 60°C, 0.7 atm N_2 atmosphere for solvent evaporation as shown in Figure 3.3. The temperature for drying was increased gradually instead of high temperature exposure at once. The temperature increased from 60°C to 90°C by 1.5 hours periods and membranes were dried at 90°C for 2 days. Thicknesses of the selective membranes were measured by a micrometer.

Mixed matrix membrane preparation:

Blending and casting was used. Prior to addition the fillers were dried at 250°C for 2 days. Same casting method steps were followed for mixed matrix membrane preparation as neat membrane preparation except after the polymer solution were filtered, dried filler added directly to the casting solution as denoted in Figure 3.3 and 3.4. To obtain a homogenous distribution of filler particles and to prevent agglomeration, the solution was left for vigorous mixing on a magnetic stirrer for 24 hours at room temperature. Before drop casting into the Petri Dish, solution was ultrasonicated (Branson 2510, 40 kHz) for an hour to make sure that the all filler particles are dispersed homogeneously and to minimize the agglomeration of particles.

Membranes having nonuniform thicknesses were obtained by aforementioned casting procedure which was more evident for PBI/Zeolite 3A. Therefore, alternative method was utilized to eliminate the nonuniform distribution of fillers. In this method, the casting solution concentration was increased by evaporating the solvent before drop casting. Because casting solution viscosity prepared by 2wt.% polymer was low and fillers were tend to precipitate. Furthermore, when membranes peeled off from Petri Dish after evaporation, heterogeneous structures were evident. Hence, to prevent the precipitation of fillers, casting solutions were left to a controlled evaporation at 140°C by using the set up shown in Figure 3.2, except condenser and cryostat, until the polymer solutions concentration reached to 8 % under vigorous stirring. Then, 25 wt.% Zeolite 3A or 20 wt.% SAPO-34 filler was added and the solutions were stirred for one more day. Before drop casting, solutions were ultrasonicated for an hour. Concentrated solutions were evaporated inside a vacuum oven at 90°C, in 0.7 atm N_2 environment. Casting solutions were evaporated by increasing the temperature step by step to 90°C from 60°C. But after solvent evaporation no further improvement was observed for both types of membranes especially for PBI/Zeolite 3A membrane. Even this concentrated casting solution was not enough to obtain homogenous membrane structure. As a consequence, this method was no longer used and solutions were casted by using 2wt.% solutions.

After obtaining both neat PBI and mixed matrix membranes additional heat treatment, annealing was applied on membranes. Two types of heat treatment were employed throughout the study:

1. In-oven annealing: Since when annealing was applied without metal frames, membranes twisted. Detached membrane thin films were placed between wire meshes, which were like thin metal frames, as shown in Figure 3.3. Furthermore, instant temperature changes during removing from evaporation oven, peeling and putting into annealing oven caused twisting of membranes. These metal frames act as a support for membranes throughout annealing process and its frame structure enable the residual solvent evaporation. After evaporation, peeled membranes were immediately put into an oven at 120°C. Membranes were in-oven annealed at 1 atm for 10 days. In order to prevent twisting of membranes, they were left cooling in oven until the temperature decreases to room temperature. A desiccator was used to keep the prepared membranes at room temperature.

Even though, metal frames were used, in many cases the final product had a twisted shape. This problem could not been prevented for in-oven annealing process. Consequently, when membranes tried to be placed into membrane module (Figure 3.5), some of them were fractured even before gas permeation testing. Some membranes prepared after a long period could not been used.

A summary of membrane preparation procedure for both membranes types are given in Figure 3.4.

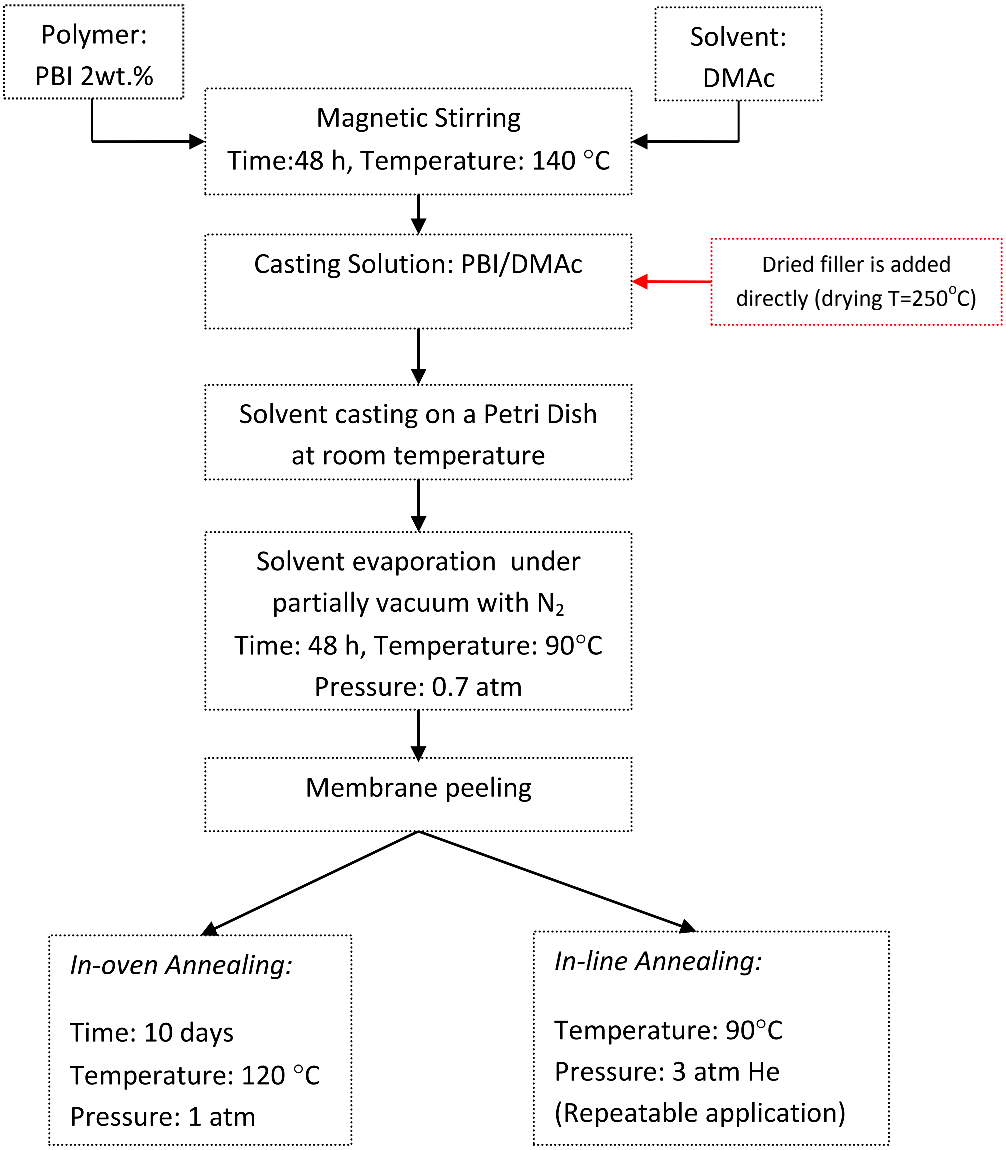


Figure 3.4: Flow chart of the neat PBI and PBI/filler membrane preparation procedure

2. In-line Annealing: Alternatively, in-line annealing was employed on the membranes using the experimental set-up shown in Figure 3.6. The annealing was carried out directly inside the membrane module. In this method membrane removed from evaporation oven was placed into the module. Temperature of the system was set to 90°C. After the system was ready, vacuum was employed on both permeate and feed sides of the system. Inert, non-interacting helium gas, which has smaller kinetic diameter (0.26 nm) compared to testing gases, was employed as feed gas at 3 atm pressure when the permeate side was at vacuum. During annealing pressure versus time data was collected. After 8 to 12 hours these data was used to calculate the permeability of helium gas. Actually, series of permeation tests were carried out by helium for long periods of time. Annealing was completed when permeations of helium gas were close in two consecutive permeability measurements.

3.3. Membrane Characterization:

3.3.1 Thermal Characterization:

Differential Scanning Calorimeter (DSC) Analysis: Thermal transition behaviors of prepared membranes were recorded on Mettler Toledo DSC 1 STAR System. A piece of membrane was placed into DSC pans and heated from 25°C to 550°C at a rate of 10°C/min in N_2 purge. Two consecutive runs were performed. After first heating the samples were quenched to room temperature and reheated to 550°C. The second run was used to estimate the glass transition temperatures of membranes via DSC.

Thermal Gravimetric Analysis (TGA) Analysis: Perkin – Elmer Pyris Thermal Gravimetry Analyzer and Mettler Toledo TGA/DCS 1 STAR System were used to determine thermal properties and the amount of entrapped solvent and water within membranes. Small piece of sample was heated from 25°C to 975°C at a N_2 flow of 10 ml/min ramped at 10°C/min.

3.3.2 Scanning Electron Microscopy (SEM) Characterization

Two scanning electron microscopes (FEI Quanta-400 F and Leo Supra 35 VP Field Emission SEM) were used to examine the morphology of prepared membranes. Prior to image acquirement, samples were prepared by fracturing the membranes in liquid nitrogen to keep the structure unaltered. Fractured membrane samples were placed in a sample holder by using a carbon tape and coated with gold/palladium while working with FEI Quanta-400 F and coated with carbon while working with Leo Supra 35 VP Field Emission SEM in order to produce a conductive layer. Cross sections of vertically placed membranes were analyzed.

3.3.3 Gas Permeability Measurements

Experimental Set-up

Single gas permeation measurements across the membranes were carried out using the set-ups assembled for flat sheet membranes previously by our research group [74, 75, 101] as given in Figure 3.6. Permeation cell (membrane module) sown in Figure 3.5 has two compartments which are separated by a membrane. A commercial module stainless steel Millipore filter holder (Millipore, part no. XX45 047 00) was utilized throughout the study containing double Viton O-ring seals.

Two different set-ups were used during the study which employs the same operating principle. First set-up was heated by using a wrapped heating tape (Cole Parmer, Barnstead/Thermolyne) having thermocouple to monitor the temperature. The pressure increase in the permeate side was followed by using MKS Baratron (0-100 Torr, 0.01 Torr sensitivity) pressure transducer. The dead-volume which is the volume occupied from the permeate side of the module to the pressure transducer was 22cm^3 [75].

In the second set-up heating was provided by placing the membrane module inside a silicone oil filled bath which was on a heater. The bath was insulated in order to keep the temperature at a constant value. A thermocouple was put into the silicone oil bath to measure the temperature. Permeate side pressure increase was measured by pressure transducer (BD Sensors, DMP331, 0.001 bar sensitivity 0–4 bar). The dead-volume was 7.1 cm^3 [74].

For both set-ups membrane module has effective membrane area of 9.6 cm^2. Set-ups were evacuated by using a vacuum pump to degasify the system. (Model E2M5, Edwards High Vacuum Pump)

In-oven annealed membranes (MB1-MB8) were tested by using first set-up and for testing the rest of the membranes second set-up was utilized.

Single gas permeabilities studies were evaluated by hydrogen and carbon dioxide gases having high purities (> 99%). These gases were supplied by OKSAN.

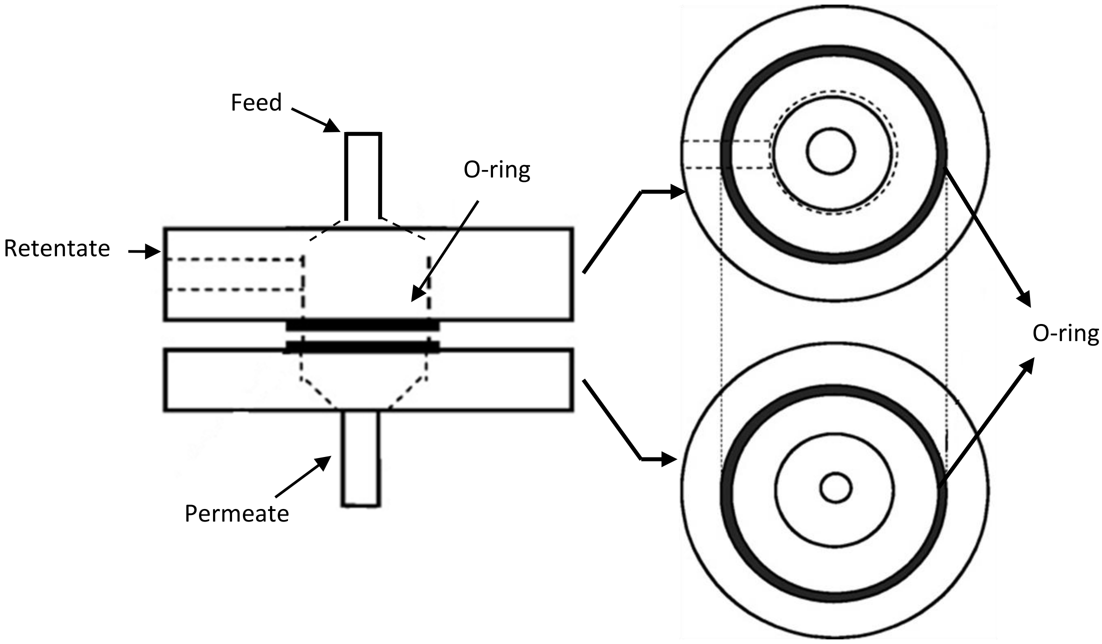


Figure 3.5: Schematic drawing of Millipore Filter holder

Experimental Procedure

Constant volume variable pressure method was utilized. Before a membrane was placed into the module, its average thickness was measured from different point of round cut film by a micrometer. The gas permeation measurements were conducted at 35°C in the first set-up and conducted in temperature range of 35-90°C in the second set-up. Both heating and cooling of the membrane module was carried out at slow rate. Heating and cooling was applied under atmospheric pressure.

In the beginning of the experiments initially, the temperature of the measurement was set to a constant value and after the temperature had reached to the desired value both upstream and downstream compartments of the module and gas tank was evacuated by using a vacuum pump for 1 to 3 hours until a residual gas free membrane was obtained. Then, pressurized gases were fed to the gas tank. Constant volume-variable pressure method relies on maintaining a higher constant pressure of upstream (feed) which was 3 atm in the experiments and measuring the gas flow through the membrane of known area and thickness. The downstream (permeate) side was kept at vacuum in the beginning of the measurements to create a transmembrane pressure difference. By the help of a needle valve the feed was sent to the module. Because of the pressure difference between feed and permeate sides, the gases began to transport through the membrane. Since a dead-end operation was applicable for the system, the gas molecules passing through the membrane was collected at the permeate side. The pressure of the permeate side was evaluated with time and this evaluation was measured by a pressure transducer and recorded via computer. The recorded raw data was put on a permeate pressure versus time plot. The steady state slope of this plot was used to determine the permeability.

The same protocol has been followed for neat and MMMs.

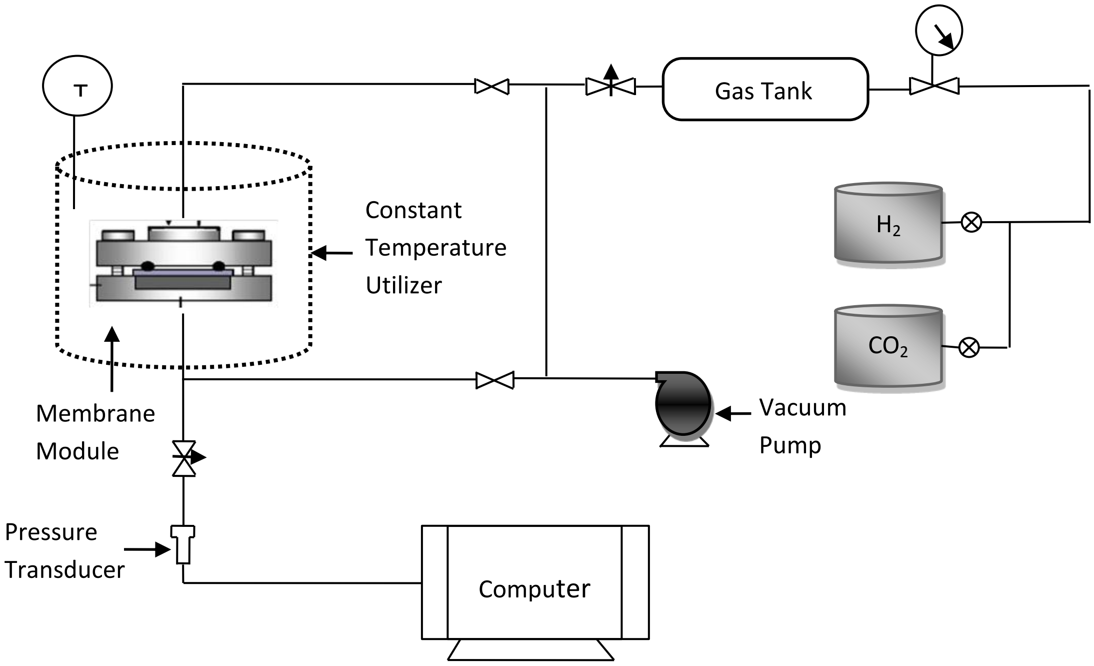


Figure 3.6: Schematic representation of experimental set-ups

The thermal stability of the membranes was evaluated by testing gas permeation performance of membranes at different temperatures. In the first set-up the measurements were done in the order of H_2 and CO_2 at 35°C and the measurements were repeated for several times until a stable performance for both gases were achieved. Between two consecutive measurements the system was evacuated but the duration of evacuation was changed according to the time of measurement. After hydrogen tests 1 hour evacuation, after carbon dioxide tests 3 hours of evacuation was applied.

In the second set-up the order of the tests was different. Tests were carried out with the same gases for several times until a stable permeation values were obtained for the specific membrane at a constant temperature. Then, the gas was exchanged and same testing protocol was followed. Only after stable permeation rates were calculated for both gases consecutive hydrogen and carbon dioxide measurements were done. If the results were consistent with the previous ones, temperature increased to 50°C, 70°C and 90°C slowly and same measurement steps were utilized at each temperature.

Permeability and Selectivity Calculations

After pressure versus experiment time data was obtained the permeabilities, selectivities, and finally, activation energies (E_a) of the experiments were established. Calculation steps for permeabilities were given in detail in previous studies of our group [74-75]. Pressure rise in the permeate side with respect to time were utilized to calculate permeability and selectivity.

Activation energies of the tested gases were obtained by;

$$P = P_o \times exp\left(\frac{-E_a}{R \times T}\right)$$

The slope of the graph demonstrated by lnP versus 1/T data gives E_a which is reported in terms of kJ/mol.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Membrane Characterization

4.1.1 Visual Characterization

Effect of preparation parameters on the separation performances of membranes have been the focus of many researches [57, 76-83]. Casting solution concentration is one of the important factors which has to be determined carefully in the beginning of the study. Hacarlıoğlu et al. [83] investigated the effect of solution composition on gas permeation performances of polycarbonate membranes by preparing 3, 5, 7, 8.5, 10, 12, 15 w/v % casting solutions. Decline in gas permeations of all tested gases including Ar, CH_4, CO_2, H_2, N_2 and O_2 were observed via increasing casting solution composition. When gas separation PBI membranes studied in literature were examined, maximum 7 wt.% casting solution was prepared in laboratory conditions [44-47, 63]. In some of the studies, higher concentration solutions were used for casting the membranes, but these solutions were received directly from suppliers [48, 61].

In this study, to elucidate the optimum polymer concentration 2, 5, 10 wt.% concentrations were tried to be prepared by PBI-1. Toward this purpose first 10 wt.% polymer solution was prepared. But, it was realized that stirring and heating under atmospheric conditions were not enough to dissolve this commercial polymer [63, 106-109]. Then it was decided to heat the solution on a hot plate to 100^{o}C. After 4 days no apparent dissolution was obtained. Even decreasing the concentration to 5 wt.% was not enough. Besides, because of the high viscosities of these solutions, it was very hard to filter the undissolved polymer via filter paper. As a result the casting solution concentration was lowered to 2 wt.% concentration. Additionally, a new setup was assembled as described in the Section 3.2 to lower the dissolution time and to provide homogeneous heating. But the dissolution problem still continued at this concentration because of the structure of these commercial polymers. Yet low viscosities of the solutions prepared at this concentration provided easier filtration by filter paper.

According to these observations in this study membranes were prepared by using 2 wt.% polymer. The viscosity of the solution was low. Therefore, instead of blade casting [71-75], drop casting into a Petri Dish was employed as shown in Figure 3.3.

To solve the major dissolution problem, which continues even at 2 wt.% concentration, 1 wt.% LiCl was added to the solvent-polymer mixture and the same solution preparation procedure was followed as described in Section 3.2. The amount of LiCl was adjusted by examining the studies done in literature [106-108]. When LiCl is used, remaining part of the salt should be removed after obtaining the membranes. Washing with hot deionized water was utilized to remove the salt. During washing in hot deionized water, twisting of the membranes were observed. The only reason for twisting may not only be LiCl addition, because throughout the study this problem continued except for LiCl free neat membranes. Moreover, in annealing step twisting was continued. In literature, it was suggested that the minor amount of this material ease the dissolution of PBI by breaking the agglomerated parts and it prevents inter and intramolecular hydrogen bonding using Cl^- ions [106-108]. During the preparation of casting solution after drying the undissolved material, white salt particles were apparent between undissolved polymer particles. This indicated that LiCl salt did not dissociate into its ions completely to disturb the chain packing of PBI. Remaining salt particles were filtered and further washing by hot deionized water was done to remove all residual salt particles on the membranes. LiCl addition had no significant effect on polymer dissolution. Moreover, by washing and drying very fragile thin films were obtained. Consequently, these thin films could not be used as a membrane and LiCl addition method was eliminated.

Another problem which was encountered during casting solution preparation for mixed matrix membrane production was based on the large particle sizes of the fillers. Two different types of fillers were used. Zeolite 3A had average particle size of 5 µm and SAPO-34 had average particle size of 200 nm. 25 wt.% Zeolite 3A and 20 wt.% SAPO-34 was added to the 2 wt.% polymer solutions. The concentration of the polymer solution was low. Consequently, even vigorous stirring was applied before drop casting, precipitation of large particle size filler at the bottom of the Petri Dish during evaporation occurred. This precipitation was visually observed especially for PBI/Zeolite 3A membranes after they were removed from Petri Dish.

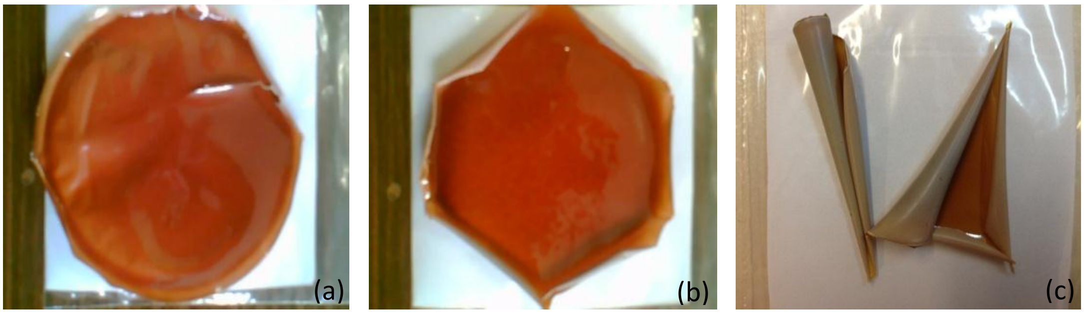


Figure 4.1: In-oven annealed membranes (a) Neat PBI membrane, (b) (c) PBI/Zeolite 3A membranes

Figure 4.1 shows the surface photographs of the in-oven annealed membranes. In Figure 4.1b and Figure 4.1c the twisted parts of the membranes have white bottom side, comprising the zeolite rich phase. But top of the membrane has a brown color, comprising the polymer rich phase.

To overcome precipitation, instant heating in oven and casting into a larger Petri Dish were tried. It was thought that by instant heating at high temperature, solvent evaporation would be achieved faster by restraining the precipitation. High temperature exposure provided faster evaporation. But as the viscosity of the solution was increased shrinkage of the solution was evident. Possibly, removal of solvent molecules caused polymer chains to pulled back together and lost flexibility. Finally, a thin film comprising only a small part of the Petri dish was obtained. Thus, stepwise temperature increased was utilized to 90°C from 60°C. But employing slow solvent evaporation increased the process duration and consequently, large zeolite particles precipitated at the bottom of the Petri Dish. Furthermore, larger Petri dish casting was employed to increase the surface for evaporation and to obtain thinner films. Same shrinkage problem was apparent. Eventually, it was decided to increase the casting solution concentration via evaporation on the hot plate before addition of fillers [109]. By this method a casting solution having higher viscosity can be obtained and during solvent evaporation the movement of fillers to the bottom may be decelerated. The PBI solution was concentrated to 8 wt.% and mixed with filler. The solution with filler was cast. A short period of time was enough to produce thin film because most of the solvent was evaporated at pre-evaporation step. But even this amount of concentrated solution was not sufficient to obtain homogeneous membrane particularly for PBI/Zeolite 3A mixed matrix membrane.

The prepared membranes were very fragile after in-oven annealing. The fractures can be seen in Figure 4.1. Metallic frames were used to prevent twisting as shown in Figure 3.3, but membranes still had tendency for bending and twisting after removed from the oven.

Alternatively, in-line annealing method was employed to prevent structural changes during the annealing and to investigate the influence of in-line annealing method on membrane performances. As shown in Figure 4.2 after solvent evaporation the obtained membranes were easier to handle. Possibly, due to softer structure coming from the residual solvent remained in the membranes. As a result, in-line annealed membranes were placed into the membrane module successfully, eliminating the issues occurring because of twisting.

Figure 4.2: In-line annealed (a) Neat PBI membrane, (b) PBI/Zeolite 3A membrane top side, (c) PBI/Zeolite 3A membrane bottom side after solvent evaporation

PBI/SAPO-34 membranes were produced only by using in-line annealing. To surpass the difficulties arisen in PBI/Zeolite 3A membrane production, smaller particle size SAPO-34 was used and the amount of filler was decreased to 20 wt.%.

4.1.2 SEM Characterization

Scanning electron microscopy (SEM) analysis was carried out to investigate the morphology of the MMMs. The SEM images of in-oven and in-line annealed PBI/Zeolite 3A and PBI/SAPO-34 are shown in Figure 4.3 to Figure 4.5 and rest of the micrographs are given in Appendix C. In Figure 4.3 left side image was obtained via carbon coating of the samples and the rest of the samples were gold/palladium coated.

Defects or huge voids were not observed in SEM images, which reveal good polymer-filler interaction. Channel like structures present in Figure 4.3 and Figure 4.3 may come from the elongation of polymer during breaking in nitrogen. Karatay et. al. [71] obtained similar observations in their study. In practice, it is desired to obtain void free structures to obtain a selective membrane.

It is evident from Figure 4.3 and 4.4 that no uniform dispersion of Zeolite 3A was obtained in PBI. Separate zeolite rich layers were observed at the bottom of the membranes and asymmetric membranes were produced. On the right sides images the upper part is the zeolite-free polymer phase and the lower part is zeolite-polymer phase. The reason of this structure could be low evaporation rates as mentioned in Section 4.1.1. Because the final evaporation temperature (90^{o}C) is lower than the boiling point of the solvent DMAc (165°C). The evaporation rate may not be enough to hinder the movement of large zeolite particles inside low viscosity casting solution to the bottom of the Petri dish during evaporation. This may lead to the precipitation of particles at the bottom [111].

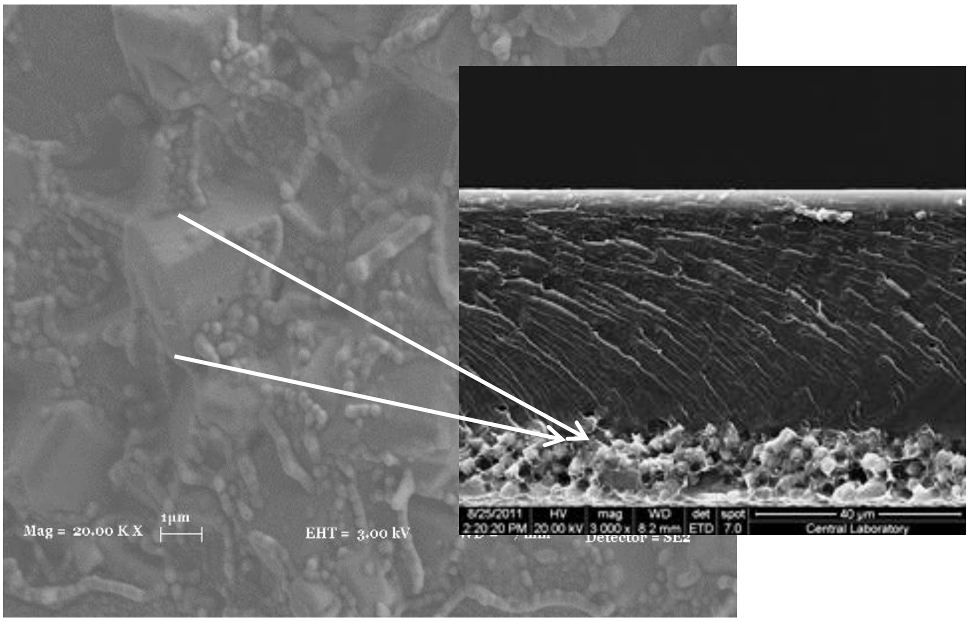


Figure 4.3: SEM images of cross section of 25 wt.% loaded in-oven annealed PBI/Zeolite 3A membrane

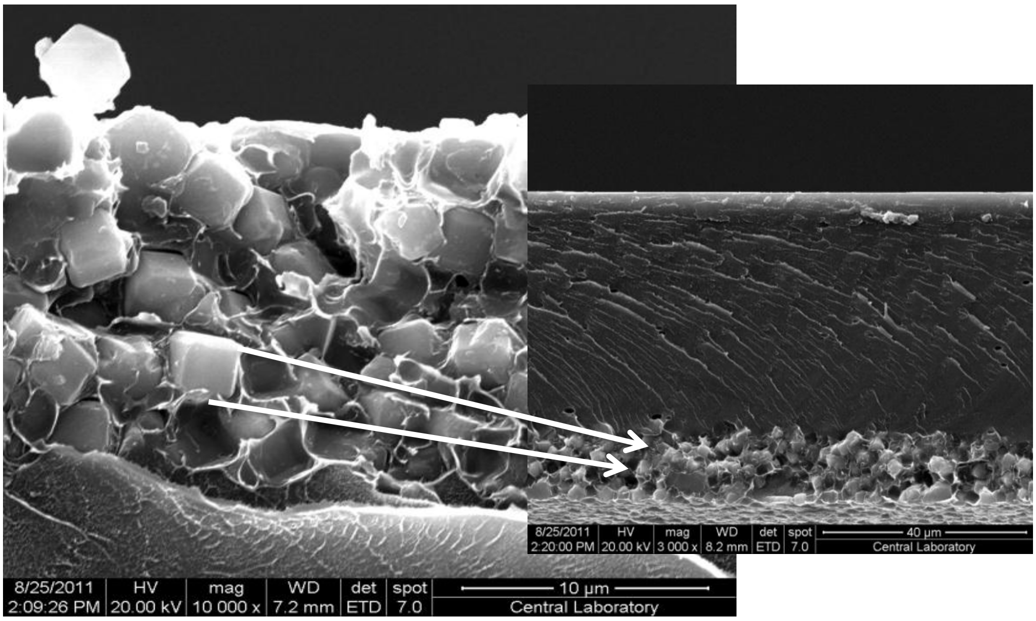


Figure 4.4: SEM images of cross section of 25 wt.% loaded in-line annealed PBI/Zeolite 3A membrane

Phase separated PBI/Zeolite 3A membranes, produced by in-oven annealing, were very fragile and they disintegrated very easily upon handling which was mentioned previously in Section 4.1.1. SEM images in Figure 4.3 and 4.4 give more detailed information about this issue. Flexible polymer matrix was glassified by solvent removal but not the same change was occurred for zeolite phase as a result very fragile and twisted thin films were obtained. They were hard to manage during gas permeation measurements and finally fractured even before placing into the gas permeation set-up. Therefore, only two of the produced in-oven annealed PBI/Zeolite 3A membranes were tested.

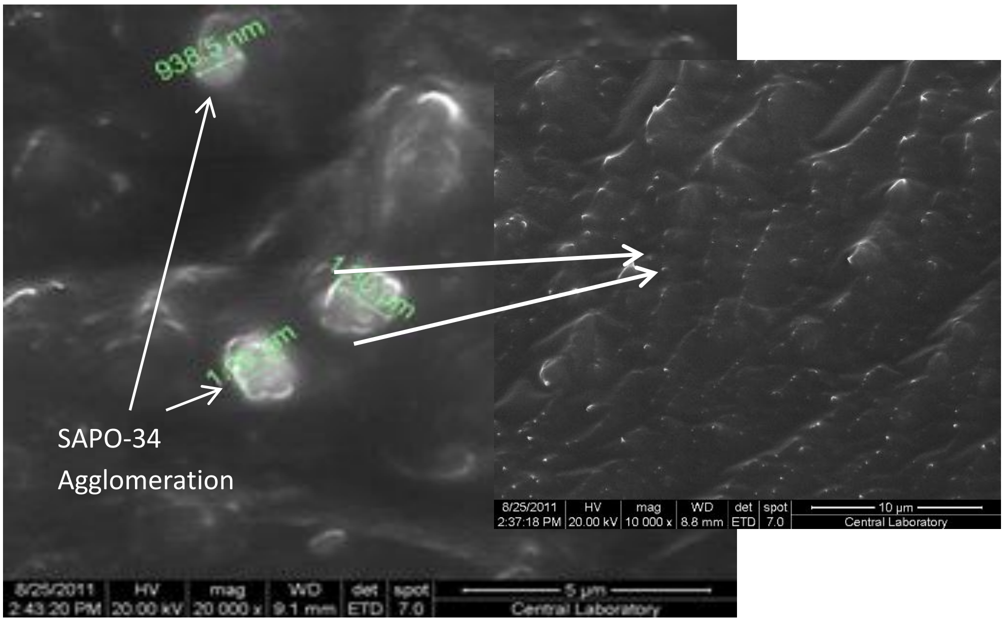


Figure 4.5: SEM images of cross section of 20 wt.% loaded in-line annealed PBI/SAPO-34 membrane

In the case of SAPO-34 addition a more homogeneous distribution was evident and particles are finely embedded in the polymer matrix (Figure 4.5). Compared to PBI/Zeolite 3A membrane this time well dispersed structure was obtained. But as observed in the figure nano-sized SAPO-34 particles were aggregated to form almost micrometer size particles that were dispersed in the polymer matrix.

By examining all SEM images shown in Figure 4.3 to 4.5, it can be said that no visible, huge interfacial voids exist. A better adhesion without any need for incorporation of a compatibilizer was succeeded for both types of MMMs opposite to other studies of our group [71, 72].

4.1.3 Thermal Analysis Results

Polymer-filler system often has a different glass transition temperature when compared to the neat polymer. By incorporation of filler into the system, improvement in separation properties with a loss in flexibility is expected for MMMs compared to polymeric membranes [12, 71, 99].

In this study DSC analysis initially carried out for polymers PBI-1 and PBI-2. Only the T_g of PBI-2 was obtained as 417^oC. This temperature was determined by taking the second derivative of the DSC thermogram as shown in Appendix B. T_g of PBI-1 could not be determined. Secondly, T_g of neat PBI and mixed matrix membranes were analyzed. But not reliable results were obtained for both types of membranes. Even neat membranes T_g values deviated from the T_g of the polymer. Solvent molecules entrapped within the polymer chains or in the zeolites possibly caused the deviations.

Small amount of solvent molecules in the polymer chains may cause plasticization [81] or antiplasticization [80] which in turn results in reduction of T_g by decreasing interchain molecular interactions or elevation of T_g respectively. Furthermore, it was speculated that the temperature range of the analysis may be changed. Because PBI has high T_g and to achieve more clear results higher temperatures may be required. Consequently, the DSC analysis results of the membranes were not discussed.

The solvent or water entrapped in membranes after annealing affects the gas permeation performance. The imprints of solvents left in the structure may influence permeation measurements. In order to characterize the remaining solvent in the structure TGA analysis were performed. The weight losses as a function of temperature are given in Table 4.1 and a representation of thermograms is given in Figure 4.6. Rest of the thermograms of individual membranes are given in Appendix D.

PBI has a T_g of 417°C and a decomposition temperature [50] of 600-630°C. In Table 4.1 up to 200°C the results show that for neat polymeric membranes, weight losses are within the range of 5-6 % but it is higher for PBI/Zeolite 3A and PBI/SAPO-34, which is almost 10 %. Underlying reason of these high values obtained for MMMs may be the hydrophilic structure of the zeolites. The total accumulated weight loss below 200°C is probably coming from the removal of residual solvent or water. Both types of annealing gave almost the same results which can be interpreted as efficient solvent removal for different kinds of annealing procedures. Significant weight losses were observed at temperatures between 200°C to 550°C for all types of membranes.

Table 4.1: Weight losses of the in-oven and in-line annealed membranes determined by TGA.

Annealing Condition	Membrane Type	Weight loss up to 200°C, (%)	Weight loss up between 200- 550°C, (%)
In-oven annealed	PBI	5.7	13.3
	PBI/Zeolite 3A	6.8	12.3
In-line annealed	PBI	5.5	15.7
	PBI/Zeolite 3A	9.8	13.6
	PBI/SAPO-34	8.5	10.5

Mixed matrix membranes weight losses are slightly higher than neat membranes regardless of annealing type. For neat membranes weight losses have similar trends. This may be attributed to higher efficiency of solvent evaporation and annealing for neat membranes. In mixed matrix membrane case possible interface creation between polymer and zeolites were occurred. Extra surfaces were created by zeolite addition. Hence solvent and water could be adsorbed by these surfaces or entrapped within the zeolites [74]. Total weight losses of in-line annealed mixed matrix membranes up to 550°C are slightly higher when compared to in-oven ones. Both time and temperature of in-line annealing was lower compared to in-oven annealing. The small variations may indicate that solvent removal was achieved slightly better for in-oven annealing.

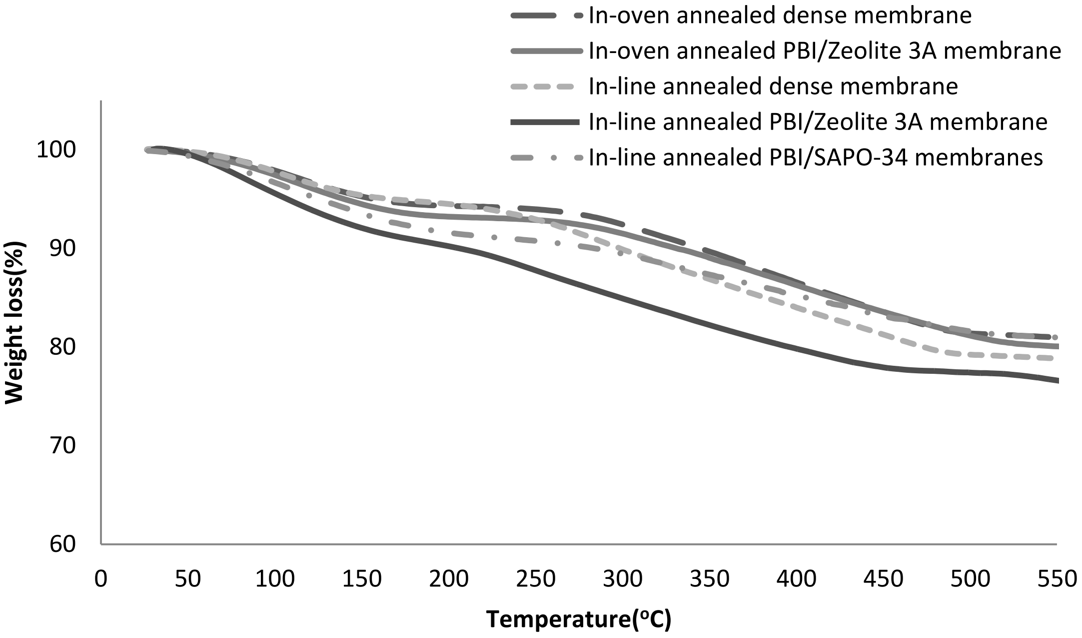


Figure 4.6: TGA thermograms of in-oven annealed dense, in-oven annealed PBI/Zeolite 3A, in-line annealed dense, in-line annealed PBI/Zeolite 3A and in-line annealed PBI/SAPO-34 membranes

Effect of the remaining solvent on the gas permeation performance of polymeric membranes was the subject of many studies, usually in accordance with the membrane preparation conditions [47, 81-85]. The studies show that the amount of residual solvent in the membranes influences the performance of membranes. Complete removal of the remaining solvent is crucial to obtain the absolute performance of the prepared membranes. The gas permeation performance depends on the preparation method [47, 85].

4.2 Effects of Preparation Methodology and Annealing on Membranes Performances

Membrane preparation conditions have paramount importance on determining the performance of a membrane. The effect of these parameters should be investigated to obtain membranes which can operate at desired conditions. Many researchers investigated the influence of these parameters on the membrane performance including the effect of residual solvent [79-82, 86].

In this study all membranes were prepared via solvent evaporation method using a casting solution of 2 w/w % polymer/solvent because of aforementioned solubility problem. The membranes were evaporated at 90°C, in 0.7 atm N_2 environment for 48 hours. The temperature of the oven was increased from 60°C to 90°C slowly. Furthermore, rising temperature caused more solvent evaporation which in turn increased the pressure in the oven. To keep the pressure at a constant value the system was evacuated during evaporation every 1.5 hour prior to temperature increase. The temperature and pressure of the operation was chosen by considering the boiling point of DMAc at that pressure ($T_{BP,\,0.7\,atm}$ = 153°C, Appendix F). Otherwise, it was thought that evaporation at a temperature close to the boiling point may cause bubbling of solvent and results in defects on the membrane.

During gas permeation measurements hydrogen was always the first gas utilized and carbon dioxide tests were done following hydrogen tests. The pressure of permeate side elevated steadily for all gases. The time of the experiment varied according to the gases, system volume and membrane type. Hydrogen which is a small kinetic diameter gas compared to carbon dioxide was always faster. As shown on Figure 4.7 the experiment time was lower for this particular gas.

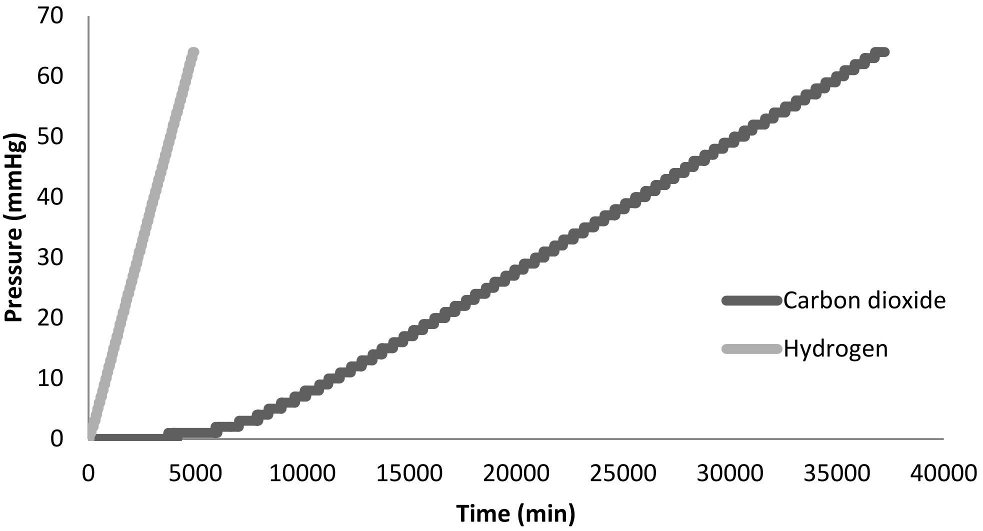


Figure 4.7: Pressure increase in the permeate side with time for neat PBI membrane

Permeabilities were evaluated by using the collected data via computer. The data was plotted on a pressure vs. time graph as shown in Figure 4.7. The straight line region of the slope, which was calculated by linear regression method, was used to evaluate permeabilities [37, 71-74].

Figure 4.7 represents a typical trend of single gas measurement for neat PBI membranes. As denoted in this figure in the beginning of the experiment when the time is equal to zero, permeation starts. But there is a certain time interval for carbon dioxide to travel from feed to permeate because of solution–diffusion mechanism. The trend shown in the Figure 4.7 is in agreement with the literature [37, 71-74]. The diffusion of bulkier carbon dioxide molecules in the membranes require more time compared to hydrogen. Hydrogen diffusion almost began immediately [73, 100].

Between two consecutive experiments the system was evacuated to make sure that the membrane is free of the tested gas. The duration of evacuation was changed according to the gas tested which was decided after a few gas permeation experiments. Membranes need more evacuation following carbon dioxide test, which is more condensable gas in the study. After hydrogen tests one hour evacuation was enough on the other hand, after carbon dioxide tests minimum 3 hour evacuation was required. This interval of evacuation was decided by monitoring the pressure increase after evacuation. Instead of instant gas permeation testing, system was left at vacuum for almost one hour and the degree of pressure elevation was followed. If sharp increase was observed the duration of evacuation was increased.

During membrane preparation high temperature heat treatment after solvent casting was employed on membranes to obtain the selective thin films. However, solvent molecules entrapped within the structure of the membranes cannot be removed completely. Even a very small amount of remaining solvent might change the performance of a membrane during gas permeation experiments [80, 81]. The solvent entrapped inside the membranes might be a governing factor in gas transport properties of membranes. Therefore, additional heat treatment called annealing was applied on membranes to extract the residual solvent.

Table 4.2: In-oven annealing conditions for some of the PBI membranes studied in literature

Reference	Membranes	Operation Conditions	Duration of operation
Sadeghi et al.[63]	PBI	100°C	24 hours
Pesiri et al. [44,45]	PBI	150°C	15 minutes
Kumbharkar et al. [39]	PBI (N-substituted)	100°C under vacuum	7 days
Choi et al. [61]	PBI, PBI/nanoporous silicate	50°C to 280°C in cyclic manner for four times	-

Within the scope of this study two different types of annealing were adopted namely in-oven and in-line annealing respectively. In-oven annealing is an operation applied on the membranes in a vacuum oven at elevated temperatures. The prepared membranes regardless of its type were placed in a vacuum oven after evaporation and annealed in nitrogen atmosphere at 120°C, 0.7 bar. Oral et al. [74] studied the effect of post annealing on PES/SAPO-34 membranes. The membranes annealed at 120°C, 0.2 bar for 24 hours. However, these membranes have lower reproducibilities. Then an additional heat treatment was applied on membranes for 7 days again at 120°C and 0.2 bar. Post-annealing at high temperature for longer durations improved the performances and also stable membranes performances were obtained. For a comparison Table 4.2 depicts examples for in-oven annealed PBI membrane from the literature. The membranes usually annealed at high temperatures. Therefore, in this study the membranes were annealed for 10 days at 120°C in the oven.

In industrial applications membranes should show stable performances at particular operating conditions. Hence, it is essential to study the repeatability of the gas permeation performances and reproducibility of membrane manufacturing in the study.

According to aforementioned aim in this study, the reproducibility and repeatability of membranes were tested by using the membranes prepared by same preparation methodology and keeping all the experimental parameters of gas permeation measurements constant.

Table 4.3 gives the permeability and ideal selectivity results for in-oven annealed neat PBI and PBI/Zeolite 3A membranes tested at 35°C. The data of gas permeation measurements of all tested membranes are tabulated in Appendix E. Membranes were tested in the order of hydrogen and carbon dioxide consecutively. The differences between the first and later runs are evident at Table 4.3. The results depicted that usually, the first gas permeability measurement for both gases, especially for hydrogen, were lower than later measurements. But the standard deviations are low. After first run the performance of the membranes were stabilized and repeatable results were obtained. This may come from the trace amount of solvent entrapped in the membrane structure [80, 81] or instable membrane structure even after annealing. When all gas permeation results are examined these inferences were corroborated. Later gas permeation runs are more consistent with each other especially for neat PBI membrane (2) and PBI/Zeolite 3A membrane (1). Densification after solvent removal may cause stiffness in polymer chains and retarded segmental motions. Moreover, the difference in the consecutive gas permeation tests could be a result of nonuniform densification of membranes during in–oven annealing. This problem causes uneven thicknesses throughout produced membranes. Average values for membrane thicknesses given in table were calculated by measuring the thicknesses at different parts of the round cut membranes. Consequently, eliminating the first gas permeation runs when working with in-oven annealed membranes, were found to be advantageous.

Table 4.3: Repeatability results of the in-oven annealed neat PBI and PBI/Zeolite 3A membranes tested at 35°C

Membrane	**Run**	**H_2 permeability**	**CO_2 permeability**	**Ideal Selectivity**
Neat PBI Membrane (1) (avg. thickness=60 µm)	1	3.76	0.63	5.97
	2	4.77	0.71	6.72
	3	4.45	0.57	7.81
	4	3.82	0.66	5.79
	5	4.86	0.59	8.24
	Avg.	4.33	0.64	6.76
	Std. deviation	**0.80**	**0.06**	**1.09**
Neat PBI Membrane (2) (avg. thickness=62 µm)	1	5.01	0.84	5.96
	2	5.64	0.84	6.71
	3	5.80	0.88	6.68
	4	4.64	0.76	6.11
	5	5.55	0.81	6.85
	Avg.	5.16	0.83	6.25
	Std. deviation	**0.43**	**0.04**	**0.40**
PBI/Zeolite 3A Membrane (1) (avg. thickness= 75 µm)	1	5.29	0.97	5.42
	2	5.65	1.01	5.57
	3	5.70	1.03	5.53
	Avg.	5.55	1.00	5.53
	Std. deviation	**0.22**	**0.03**	**0.08**
PBI/Zeolite 3A Membrane (2) (avg. thickness= 80 µm)	1	3.74	0.79	4.73
	2	4.16	0.81	5.14
	3	3.85	0.75	5.13
	Avg.	3.92	0.78	5.00
	Std. deviation	**0.22**	**0.03**	**0.23**

In oven annealed membranes, although same casting methods were followed, regardless of the membrane type, they showed not very stable performances. In order to overcome repeatability and reproducibility problems in-line annealing was employed.

In-line annealing is a process where membranes are annealed in the experimental set-up shown in Figure 3.6. After solvent evaporation the membranes were placed in the experimental set-up for annealing using non-interacting helium gas at 90°C.The period of process with helium is shown in Figure 4.8 as a pressure versus time graph. 'V' indicates the evacuation interval. To make sure that the annealing was completed many successive test runs for extended periods of time were done with helium gas. Since, it is possible to expect the time dependency of permeation of helium throughout the membranes containing remaining solvent. This is the result of slow leaching of the remaining solvent using a gas [84]. The permeability of each run was calculated using the slope of every curve by linear regression method. Longer periods of time in the figure indicate the permeation during night.

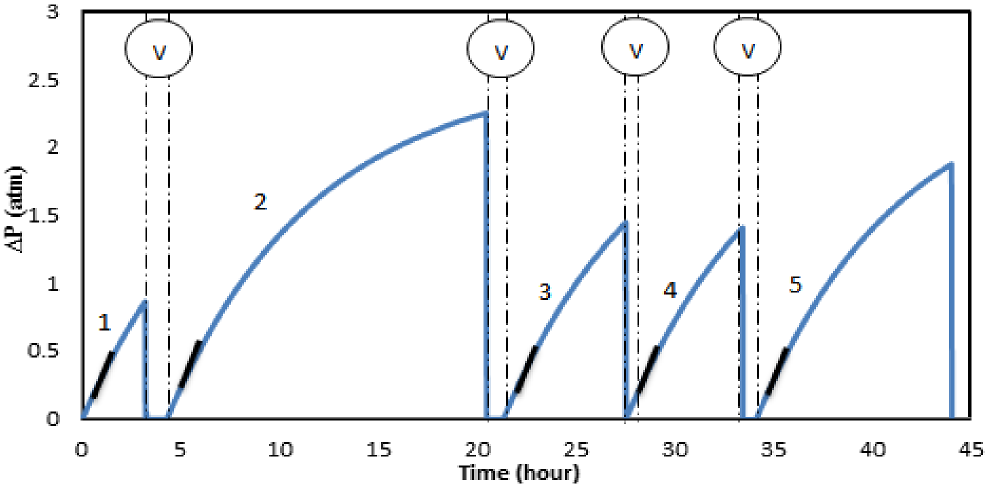


Figure 4.8: In-line annealing operation period at 90°C

The calculated slopes of the curves in Figure 4.8 were given in Table 4.4. The slopes of the curves for particular neat membrane increased in the first three runs which depicts the removal of solvent by helium transport through the membrane. During these runs a competitive transport of remaining solvent and helium gas is evident. The increase in slopes depended on the release of residual solvent. After third run almost same slopes were obtained meaning the fulfillment of the annealing process. So, gas permeation measurements were utilized.

Table 4.4: Slopes of the curves given in Figure 4.8

Slope	Values
α1	7.50E-05
α2	7.72E-05
α3	7.79E-05
α4	7.79E-05
α5	7.81E-05

Using in-line annealed membranes H_2permeation tests were done for several times until close permeability values obtained for successive measurements as shown in Table 4.5. When the results were consistent CO_2 gas was utilized for several times. After obtaining close permeability results for both gases, one more test in the order of hydrogen and carbon dioxide was done to ensure the repeatability of the results.

Table 4.5: Repeatability results of the in-line annealed neat PBI, PBI/Zeolite 3A, PBI/SAPO-34 membranes tested at 35°C

	Run	**H_2 permeability**	**Run**	**CO_2 permeability**	**Ideal Selectivity**
Neat PBI membrane (avg. thickness= 75 µm)	1	7.59			
	2	7.54			
	3	7.90			
	4	7.85	1	3.34	2.35
			2	3.31	
			3	3.37	
			4	3.40	
			5	3.42	
	5	7.79	6	3.32	2.32
	6	7.92	7	3.40	2.33
	Avg.	7.77	Avg.	3.37	2.31
	Std. deviation	**0.11**	Std. deviation	**0.04**	**0.01**
PBI /SAPO-34 membrane (avg. thickness=85 µm)	1	8.2			
	2	8.04	1	2.52	3.2
			2	2.68	2.91
	3	7.8			
			3	2.57	3.04
	Avg.	8.01	Avg.	2.59	3.09
	Std. deviation	**0.20**	Std. deviation	**0.08**	**0.15**
PBI/Zeolite 3A Membrane (avg. thickness=90 µm)		7.81			
		7.65		2.74	2.79
				3.02	
		7.61			
				3.00	2.54
	Avg.	7.69	Avg.	2.92	2.63
	Std. deviation	**0.11**	Std. deviation	**0.16**	**0.18**

Using in-line annealed membranes H_2 permeation tests were done for several times until close permeability values obtained for successive measurements as shown in Table 4.5. When the results were consistent CO_2 tests were utilized for several times. After obtaining close permeability results for both gases, one more test in the order of hydrogen and carbon dioxide was done to ensure the repeatability of the results.

In-line annealing was utilized for neat PBI, PBI/Zeolite 3A and PBI/SAPO-34 membranes. In the Table 4.5 permeability results are given. It is very easy to observe the stability of the measurements. Consecutive gas permeations of the gases were almost equal to each other. Many runs with the same gas were utilized and low standard deviation from average permeations and ideal selectivity values were calculated. In literature there is one another study done by Kruczek and co-workers [84] using in-line annealed membranes. They in-line annealed their sulfonated polyphenylene oxide membranes by using CO_2 gas and measured the permeabilities of nitrogen, oxygen, methane and carbon dioxide. Average permeabilities and standard deviations were reported by using the results of three membranes of one kind. The low standard deviation values indicate the repeatability of the measurements. In this study, the performance results indicate erasing the thermal history and suppressing the stress on the membranes were accomplished by in-line annealing. Furthermore, one other problem which would have arisen was the thickness determination. Because after evaporation the obtained membranes still contains some solvent inside them which makes them considered as wet. The final dry membrane thickness would deviate from the initial value [84]. But not a significant difference was observed in our case. Stable and repeatable performances were succeeded and reproducible membranes were obtained by in-line annealing regardless of membrane type.

Table 4.6: Comparison of in oven and in line annealed neat PBI and PBI/Zeolite 3A mixed matrix membranes at 35°C

Annealing Type	Membrane Type	H_2 permeability (Barrer)	CO_2 permeability (Barrer)	H_2/CO_2 selectivity
In-oven	Neat PBI	5.16	0.83	6.21
In-line		7.77	3.37	2.31
In-oven	PBI/Zeolite 3A	5.55	1.00	5.55
In-line		7.69	2.92	2.63

To compare the gas separation performance results of membranes Table 4.6 was prepared by using average gas permeability ideal selectivities. This table represents the performance values for both neat PBI and PBI/Zeolite 3A membranes at 35°C. The permeabilities and selectivities of in-line annealed membranes are quite different from in-oven annealed membranes. The permeabilities were enhanced conversely; selectivities were decreased by switching the annealing type.

When Robeson upper bound line examined, which is shown in Figure 2.3, to reach industrially attractive region the ideal case is moving in the direction of the arrow by improving both selectivity and permeability. But alternatively, it can be reached by either increasing the permeability or selectivity. In our case by applying in-line annealing permeabilities for both types of membranes were increased, meaning an approach to the upper bound line from horizontal direction was applied as shown in Figure 4.9. The upper bound line was drawn by using data in the article of Robeson [115]. The influence of annealing type is more evident for neat PBI membranes; carbon dioxide permeability was increased by almost four fold along with a decline in ideal selectivity. Same results are applicable for PBI/Zeolite 3A membrane; in this case almost 3 fold permeability increase for carbon dioxide is apparent. The loss in selectivity and enhancement of permeability could be attributed to the structural changes occurring during in-line annealing. Chang and co-workers simulated the molecular motion changes with the temperature on polyimide membranes. They concluded that at elevated temperatures as the remaining solvent decreases, thermal motions of the chains were altered [102]. In this study at 90°C, by inert helium permeation, the chains of the polymer may be reorganized and the performance results could be the result of increase of free volume created by helium. Furthermore, improvement in carbon dioxide permeability may support this claim. Eventually, changing annealing type had positive influence on membrane performances.

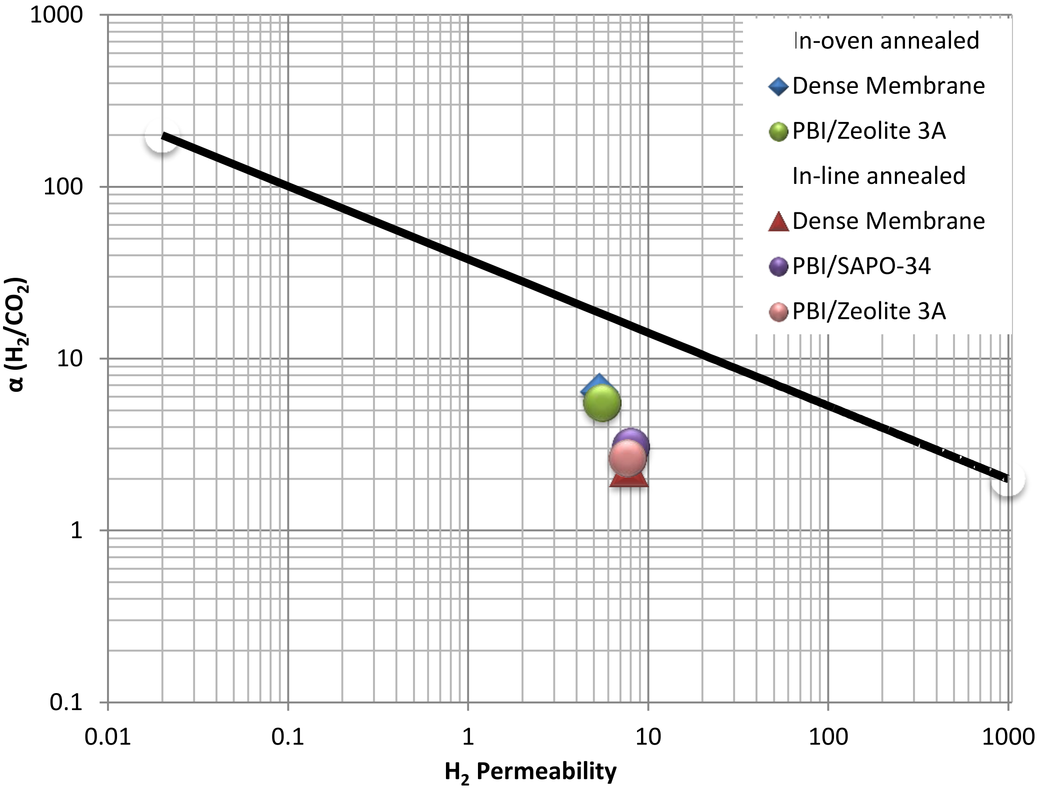


Figure 4.9: Representation of permeability and selectivity data on Robeson upper bound line at 35°C

Table 4.7: The hydrogen permeabilities and ideal selectivities of the PBI membranes studied in literature

Referance	Membranes	T (°C)	H_2 permeability	Ideal Selectivity
Tsapatsis et al. [61]	PBI (1)	35	3.0	12
	PBI (2)	35	1.5	15
Lee et al. [41]	PBI (Thermally Rearranged)	23	1400	1.1
Young et al. [52]	PBI(Crosslinked)	23	11.2	16
Berhtold et. Al. [48]	PBI/ stainless steel composite	250	4.67	43

Table 4.7 gives information about the PBI membranes studied in literature for hydrogen and carbon dioxide separation [41, 48, 52, 61]. The structures and preparation methodologies of the membranes are different from our study. The influences of these differences are evident on the performance results. Tsapatsis et al. [61] obtained the highest selectivity for H_2/CO_2 separation as 14 at 35°C by using membranes prepared via 20 wt.% casting solution. The prepared mixed matrix membranes gave almost four times higher selectivities than our membranes. In their study, they investigated the preparation conditions including casting surface, casting solution concentration and evaporation conditions. In the study they compare their gas permeation results of neat PBI

membranes with literature [52, 114]. Differences in both permeabilities and selectivities were evident. The different casting surfaces and evaporation conditions are considered to be the reason behind these differences. They mentioned that up to one order of magnitude difference may occur according to the evaporation temperature and casting surface. In the Table 4.7 neat membranes indicated as PBI (1) and PBI (2) showed different gas permeation results. Room temperature dried membrane PBI (1) permeability is almost 2 fold higher than 80°C dried PBI (2) membrane. Furthermore, by crosslinking the polymer a closer structure can be obtained and as a result formed membranes can have a denser structure. The reason of the better performance can be attributed to this denser membrane [52]. In another study done by Berhtold et al. [48] PBI composite membranes were prepared. In order to obtain the performance of the membranes high temperature permeability measurements were employed. They claimed that they produced a membrane which has a performance in the industrially attractive region of the Robeson trade-off line [53].

Table 4.8: The average permeabilities and ideal selectivities of in-oven and in-line the neat PBI and mixed matrix membranes at 35°C

Annealing Type	Membrane Type	H_2 permeability (Barrer)	CO_2 permeability (Barrer)	H_2/CO_2 selectivity
In-oven	Neat PBI	5.16	0.83	6.21
	PBI/Zeolite 3A	5.55	1.00	5.55
In-line	Neat PBI	7.77	3.37	2.31
	PBI/Zeolite 3A	7.69	2.92	2.63
	PBI/SAPO-34	8.01	2.59	3.09

Effect of filler on both in-line and in-oven annealed membranes were investigated. Table 4.8 gives the average performance results for neat PBI and mixed matrix membranes. As can be seen from the table incorporation of large particle size Zeolite 3A into the polymer matrix increased the gas permeabilities of in-oven annealed membranes along with a slight loss in selectivity. But opposite trend was observed for in-line annealed membrane. As evident from the SEM image given in Figure 4.3 and Figure 4.4 the precipitation of Zeolite 3A particles produce a different phase and the particles acted as a separate layer. In this case permeabilities were expected to increase as the sieving effect may be dominant at the bottom of the membrane and gas transport may have facilitated. Possibly, partial blockage of zeolite particles by polymer chains in the zeolite-polymer phase caused only a slight change in gas permeation performances. But, in the case of PBI/SAPO-34 membrane improvement in both hydrogen permeability and selectivity were provided. SEM images given in Figure 4.5 indicated embedded SAPO-34 particles throughout the cross-section of the polymer. Smaller zeolite particles enables more interface between polymer and particle, hence improve the performance [12]. Yet accumulated SAPO-34 particles were observed which may have decreased the amount of desired interfaces and as a results slight improvement in permeabilities was achieved especially for hydrogen. Eventually, the transport of carbon dioxide retarded. The improvement in the performance of membranes by addition of SAPO-34 can be interpreted as creation of more tortuous pathways for gases. When effect of different filler type is considered SAPO-34 addition was more advantageous.

Aforementioned studies refers that polymer state inside the membrane is fundamentally related to the amount of remaining solvent in the membrane structure. TGA results shown in Figure 4.6 revealed good solvent removal for all membranes. Moreover, it is clear that solvent extraction depends on the annealing type, time and temperature. Therefore, it is fundamental to obtain the optimum annealing conditions for prepared membranes to achieve desired gas permeation performance.

Depending on the above stated and obtained results, it can be said that our results are consistent with the literature. Choosing the suitable remaining solvent removal method, annealing, has fundamental effect on membrane gas permeation performance. Furthermore, different annealing methods influence the repeatability and reproducibility of membranes performances. Therefore, it was found that if required it is essential to change the annealing methodology. By the addition of filler the gas permeation performances were changed slightly, but it was more pronounced for in-line annealed PBI/SAPO-34 membrane. Throughout the study the best performances were obtained by using PBI/SAPO-34 membrane as shown in Table 4.5 and Figure 4.9.

4.3 Effect of Operating Temperature on Membranes Performances

Since industrial scale hydrogen and carbon dioxide separation occurs at elevated temperatures it is crucial to purify hydrogen at high temperatures to provide an integration of membranes into the system with minimum temperature penalty. The effect of operating temperatures on in-line annealed membranes was investigated by changing the temperature from 35°C to 90°C by using in-line annealed membranes.

Temperature was used as tool for optimizing the membrane performance. The gas measurements were done in the order of hydrogen and carbon dioxide throughout the tests at 35°C, 50°C, 70°C and 90°C using in-line annealed membranes. When the repeatability of results was evident at one temperature as represented in Table 4.9, further temperature increase was applied. The data of all gas permeation measurements for all in-line annealed membranes were given in Appendix E.

Table 4.9: Gas permeation performance of in line annealed neat membranes at 35°C

Membrane	Run	H_2 permeability	Run	CO_2 permeability	Ideal Selectivity
Neat PBI membrane	1	10.09			
	2	9.49			
	3	9.53			
			1	4.01	
			2	4.19	
			3	4.05	
	4	9.33	4	3.95	2.36
	5	9.51	5	3.88	2.45

According to the purpose the performances of neat PBI membranes were investigated. Figure 4.10 and 4.11 represents the permeabilities and selectivities of the given polymers at different temperatures respectively. Both figures have increasing trends for permeation rate and ideal selectivity. These results are consistent with the literature [27, 48, 111]. It is believed that for polymeric membranes solution-diffusion mechanism is applicable when talking about gas permeation. In glassy polymers relative to solubility mechanism diffusivity mechanism is more altered by temperature increase due to increased chain motion and associated kinetic phenomena [44, 110]. Therefore, smaller molecule hydrogen gas permeability is found to be more influenced from the temperature [110]. Rowe et al. [113] experienced the same results in their study. Furthermore, Pesiri et al. [44] increased the operating temperature up to 340°C. For single gas permeation measurements same behaviors was observed as our study.

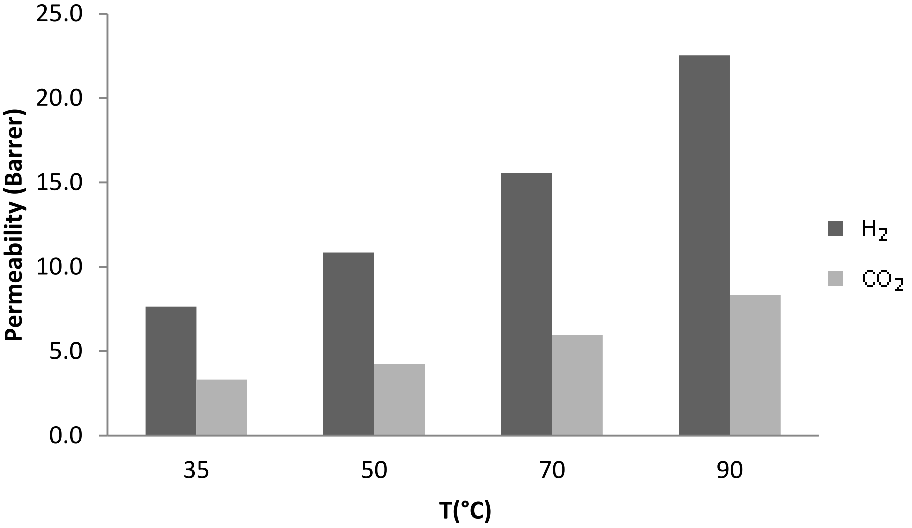


Figure 4.10: Effect of operation temperature on permeabilities of in-line annealed neat PBI membranes

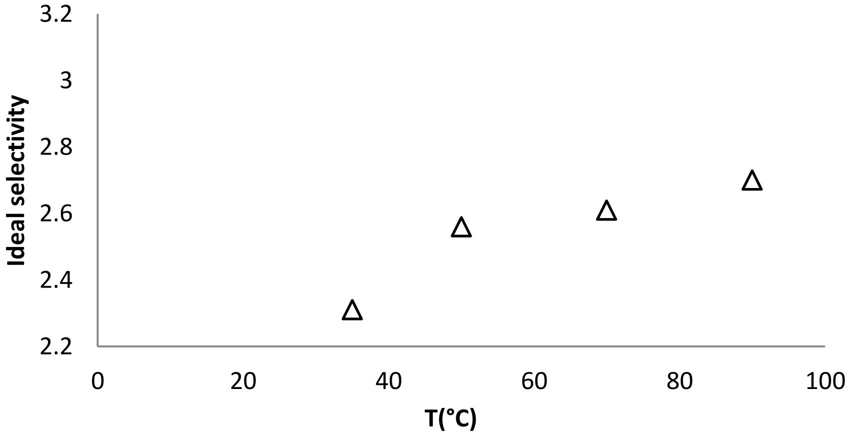


Figure 4.11: Effect of temperature on the ideal selectivity H_2/CO_2 of in-line annealed neat PBI membranes

Same gas permeation measurement method was followed for mixed matrix membranes. Figure 4.12 to Figure 4.15 represents the permeabilities and ideal selectivity data for PBI/Zeolite 3A and PBI/SAPO 34 membranes. By increasing temperature both permeabilities and selectivities were increased for all types of membranes. Diffusivity of gases shows an inverse trend to the size of the gas. Hence, in order to obtain a hydrogen selective membrane the dominant mechanism in the polymers should be diffusivity, which in turn act as a molecular size sieve [48]. Addition of both zeolites improved the gas permeation performance slightly by altering the size sieving mechanism.

The gas permeation results indicated no mismatch between two phases. On the contrary, Choi et al. [61] observed an opposite trend for PBI/silicalite membrane gas permeation performance. At higher temperatures, especially higher than 100^{o}C, decline in mixed matrix membranes performance was obtained. This was attributed to the mismatch between two phases. In our case

PBI/SAPO-34 membrane which has a more homogeneous structure possessed better performance compared to both neat and PBI/Zeolite 3A membrane.

Table 4.10: Gas permeation performance of in-line annealed neat PBI and mixed matrix membranes at 90°C

Membrane type	H_2 permeability	CO_2 permeability	Ideal Selectivity
Neat PBI	22.38	8.64	2.59
PBI/Zeolite 3A	26.54	9.10	2.91
PBI/SAPO-34	26.73	8.74	3.06

Since solubility and diffusivity gives different trends toward temperature, it is crucial to study membranes at higher temperatures. Table 4.10 contains the average performance results of neat PBI and mixed matrix membranes at 90°C. Addition of fillers provided a better performance by especially increasing the permeability of hydrogen. When the results in Table 4.10 compared with results in Table 4.3 which were performed at 35°C, influence of temperature especially on hydrogen gas can be recognized easily. These results indicate the positive effect of temperature on the diffusive mechanism of the dominant gas, hydrogen. When all in-line annealed membranes are compared PBI/SAPO-34 membrane gives the best results, by letting more hydrogen permeability and surpassing the carbon dioxide permeability to some extent.

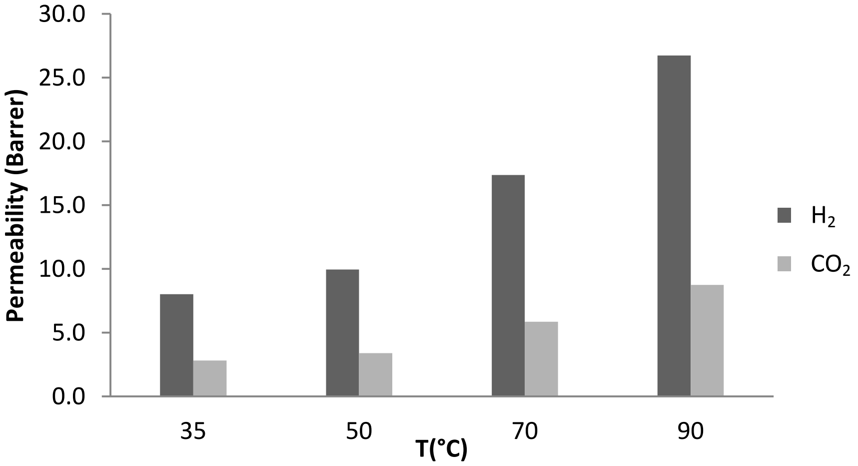


Figure 4.12: Effect of operation temperature on permeabilities of in-line annealed PBI/SAPO-34 membrane

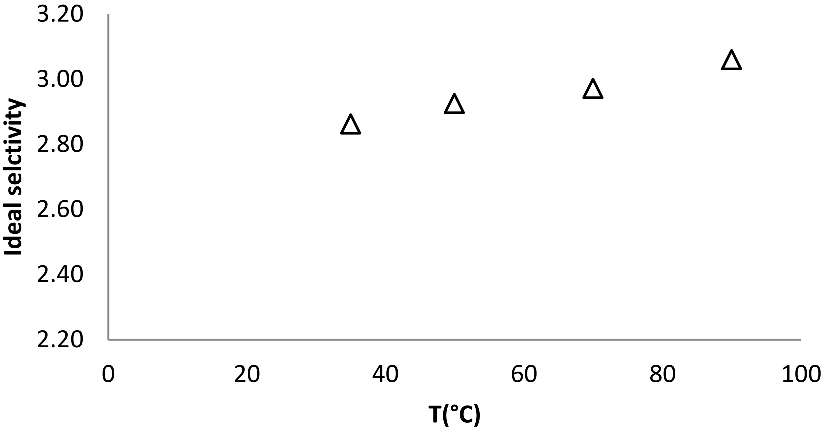


Figure 4.13: Effect of temperature on the ideal selectivity H_2/CO_2 of in-line annealed PBI/SAPO-34 membrane

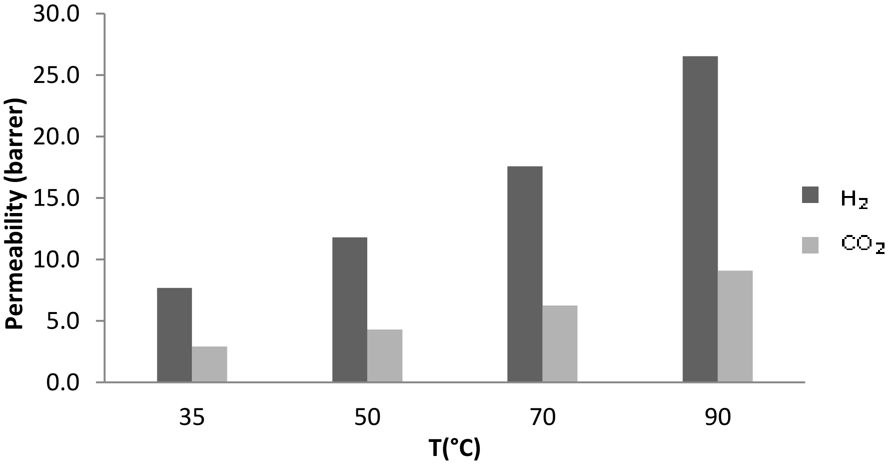


Figure 4.14: Effect of operation temperature on permeabilities of in-line annealed PBI/Zeolite 3A membrane

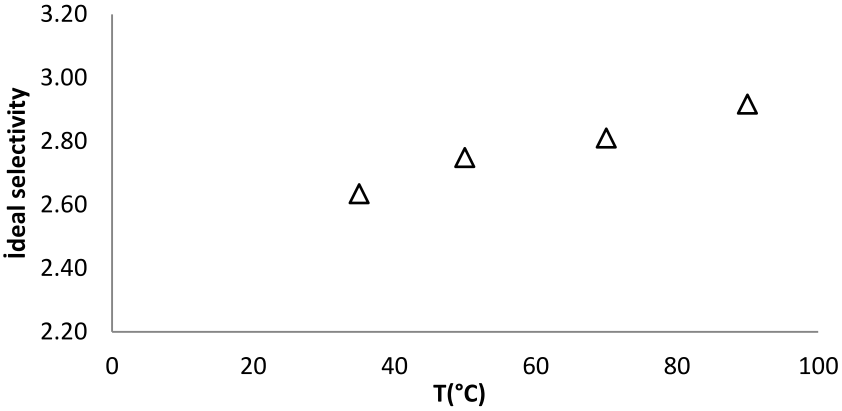


Figure 4.15: Effect of temperature on the ideal selectivity of H_2/CO_2 in-line annealed PBI/Zeolite 3A membranes

Same trends obtained for both gas permeabilities and selectivities for in-oven annealed membranes at 90°C as in-line annealed membranes as indicated in Table 4.11. Hydrogen and carbon dioxide permeabilities are increased. But it is more apparent for hydrogen which in turn enhanced the ideal selectivity of the PBI/Zeolite 3A membrane.

Table 4.11: Effect of operation temperature on permeabilities of in-oven annealed PBI/Zeolite 3A membranes

Temperature	H_2 permeability	CO_2 permeability	Ideal Selectivity
35°C	4.06	0.70	5.82
90°C	12.19	1.91	6.38

Temperature dependent permeation of a gas can be defined by using an Arrhenius type equation. The temperature dependent permeation rates were plot as shown in Figures 4.14 and 4.15. The activation energies of the particular gases were calculated and tabulated at Table 4.12.

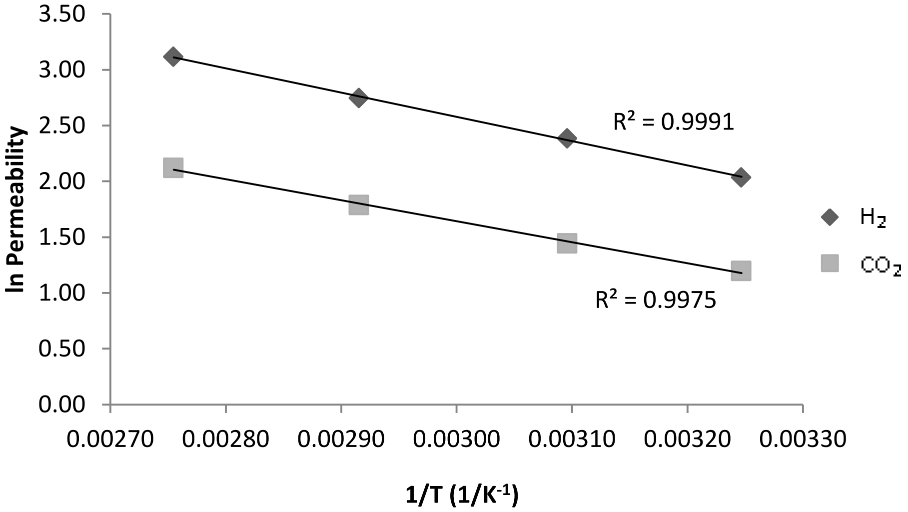
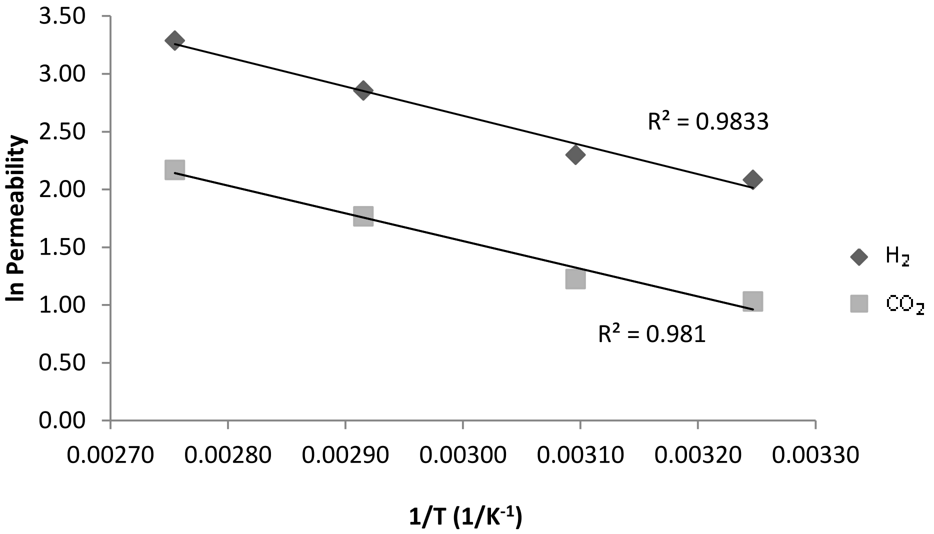
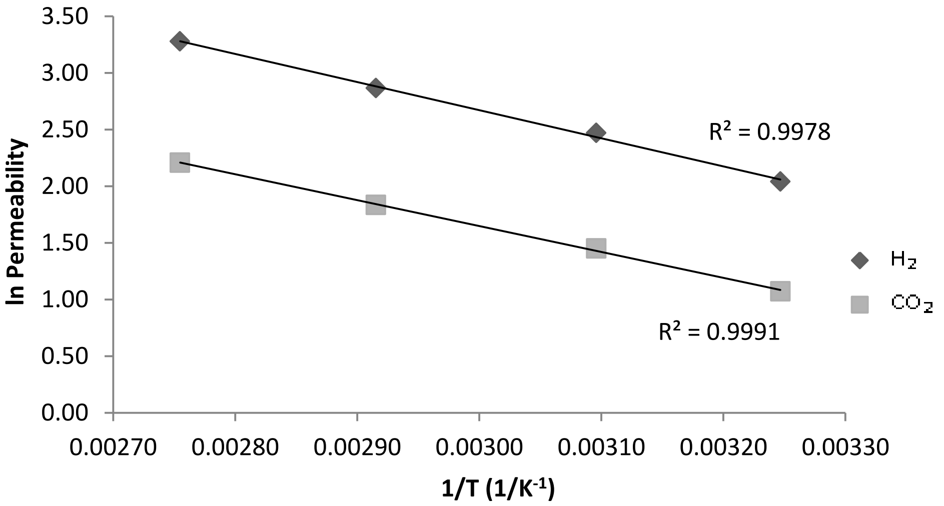


Figure 4.16: Activation energy lines for in line annealed neat PBI membarane



(a)



(b)

Figure 4.17: Activation energy lines for in line annealed (a) PBI /Zeolite 3A, (b) PBI/SAPO-34 membranes

Table 4.12: Activation energies of membranes (kJ/mol)

	Neat PBI membrane	PBI /SAPO-34 membrane	PBI /Zeolite 3A membranes
H_2	18.07	21.01	20.62
CO_2	15.65	20.82	19.03

For all kinds of membranes activation energies showed Arrhenius behavior which is evident when regression values are examined. Pesiri et al. [44] obtained similar results. However, at higher temperature hydrogen permeability became offset by selectivity especially, temperatures higher than 300^{o}C. Because they suggested that carbon dioxide permeation could have been dominant at higher temperatures. Berchtold et al. [48] tested produced PBI composite membranes temperatures up to 250^{o}C. Within temperature ranges studied the consistent gas transport mechanism was diffusivity and Arrhenius type of behavior was pronounced.

In a study of our group done by Oral et. al. [74] investigated the effect of temperature on the activation energies of H_2, CO_2 and CH_4 by using PES based membranes. The highest kinetic energy was found for methane which has the kinetic diameter and the lowest activation energy was found for carbon dioxide which is the more condensable gas for all types of membranes studied.

In this study highest activation energies are obtained for hydrogen which means this gas is more influenced by increasing temperature as demonstrated previously by gas permeation experiments. The lowest value belongs to more condensable gas carbon dioxide. The selectivity decrease with rising temperature can be attributed to the decline in solubility of carbon dioxide gas as a function of temperature. Higher activation energy values for mixed matrix membranes shows that these membranes are more sensitive to the temperature change [81, 82]. PBI/SAPO-34 membrane was the most temperature sensitive membrane according to the activation energies.

CHAPTER 5

CONCLUSIONS

In this study, the dependence of gas transport to temperature and annealing methodology were investigated. The following conclusions were extracted:

1. Solution casting concentration should be determined carefully.

2. Annealing type has a great influence on the membranes. To obtain consistent gas permeation results membranes should be in-line annealed.

3. It is been known that working at high temperatures is more advantageous for hydrogen and carbon dioxide separation. As the temperatures elevated the permeabilities of both gases increased. But hydrogen was the dominant gas in permeation in high temperatures which was indicated by the improved selectivity for H_2/CO_2.

4. All types of membranes including neat PBI, PBI/Zeolite 3A and PBI/ SAPO-34 membranes resisted up to 90^{o}C. PBI/SAPO-34 membrane has higher separation performance at each temperature and can resist up to 90 °C without any change in gas separation performance.

5. Working with smaller particle sized particles improved the performance of the membranes as a result of more homogeneous distribution.

6. Among all types of membranes PBI/SAPO-34 mixed matrix membranes had the highest activation energies. Furthermore, hydrogen had the highest activation energy regardless of membrane type.

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APPENDIX A

PARTICLE SIZE DISTRIBUTION OF SAPO-34 PARTICLES

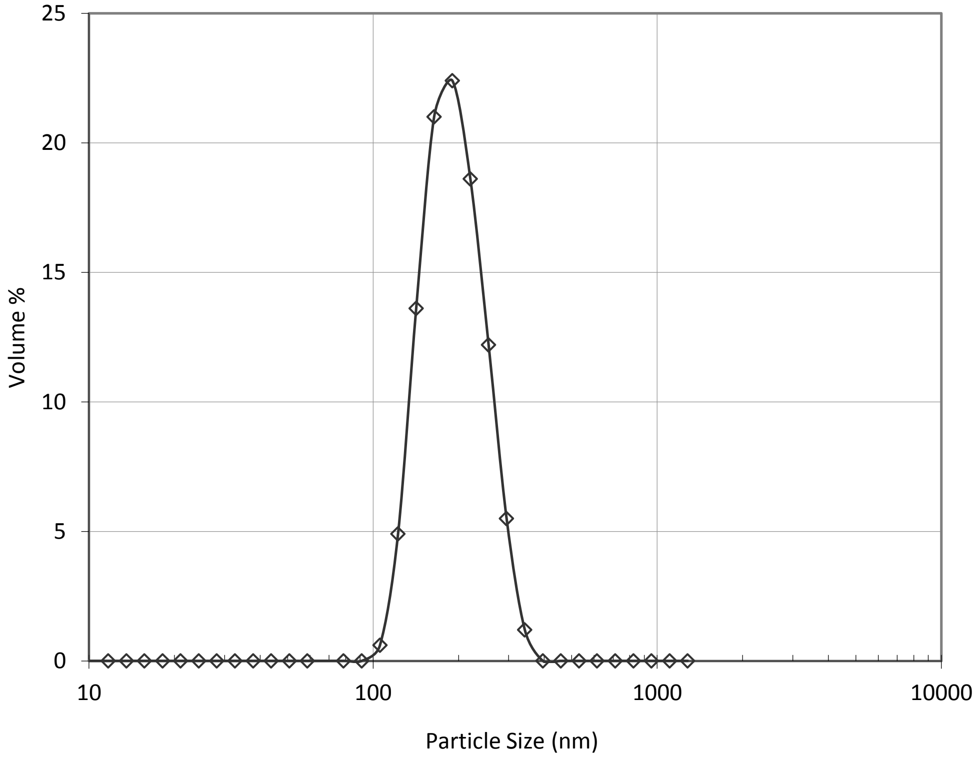


Figure A.1: Particle size distribution of SAPO-34 particle

APPENDIX B

DIFFERENTIAL SCANNING CALORIMETRY SCAN OF FUMIAN AP (PBI-2)

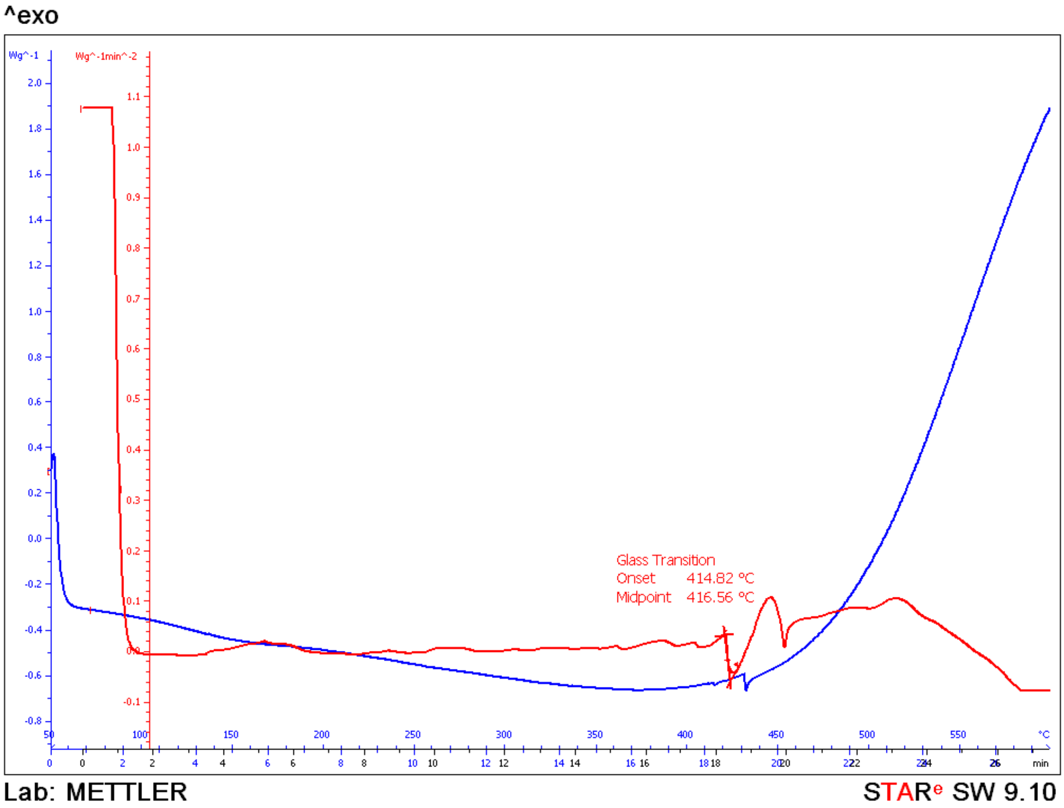
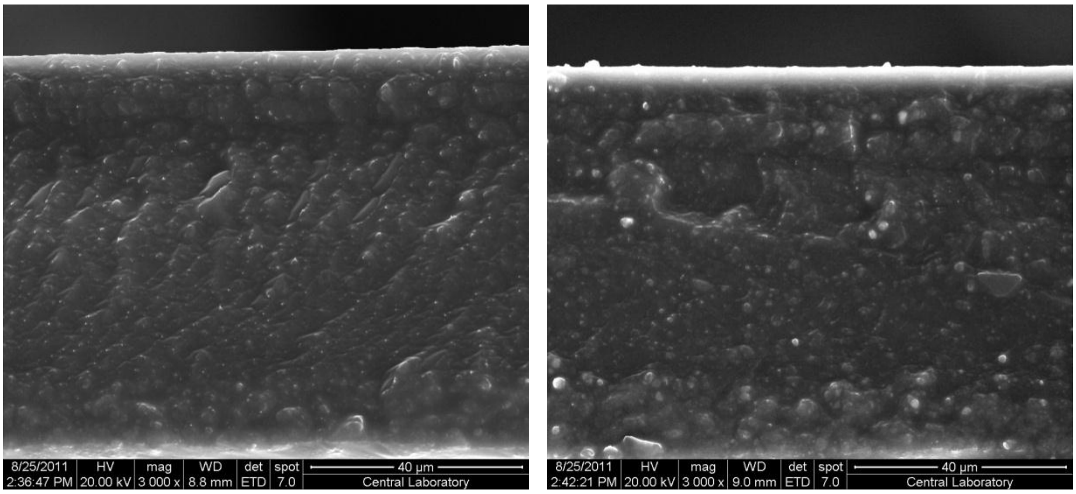


Figure B.1: DSC diagram of Fumian AP

APPENDIX C

SEM IMAGES



(a) (b)

Figure C.1: (a), (b) SEM images of 20 % w/w Zeolite 3A loaded mixed matrix membrane

APPENDIX D

TGA THERMOGRAMS

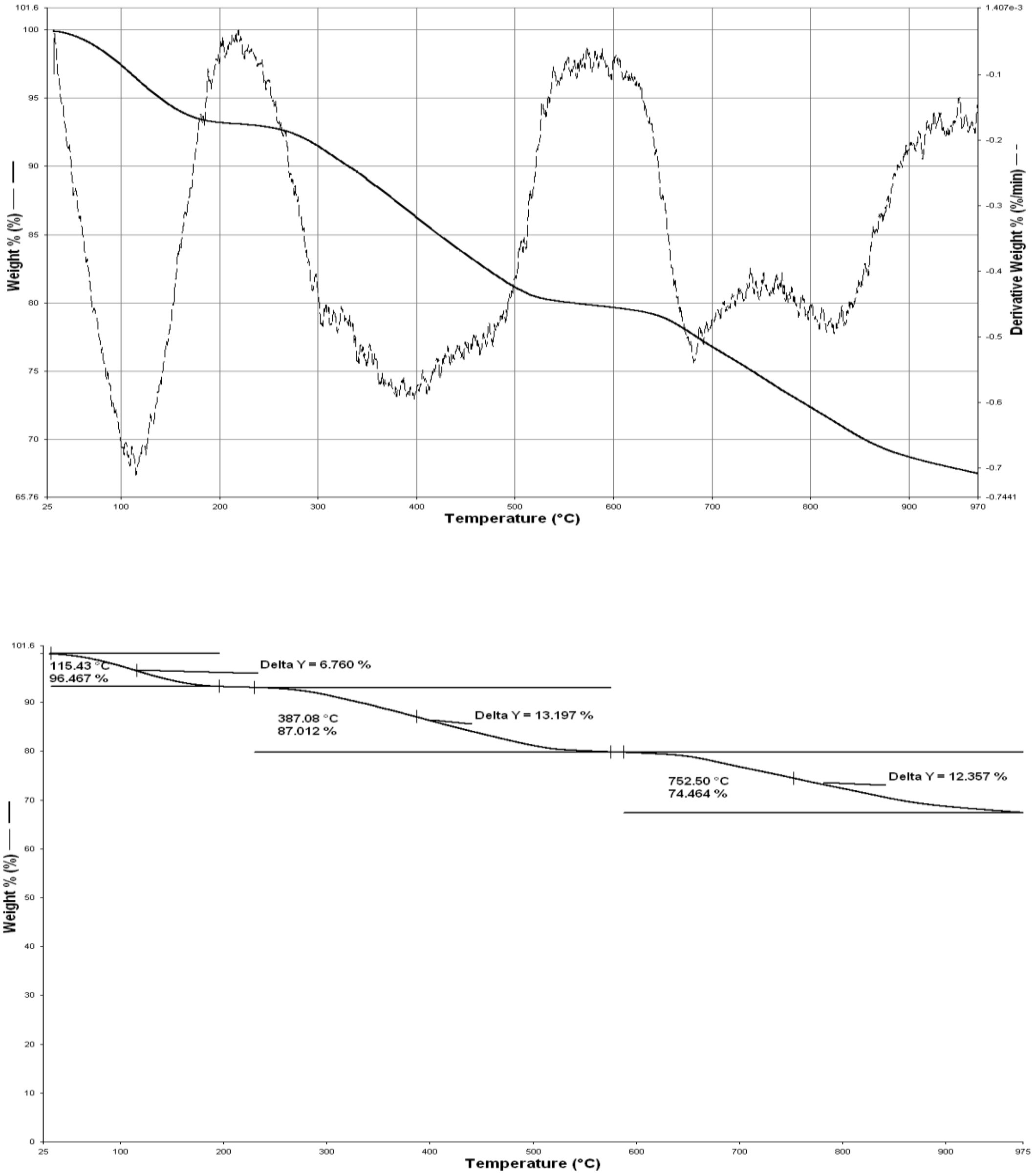


Figure D.1 TGA Thermogram for in-oven annealed neat PBI membrane

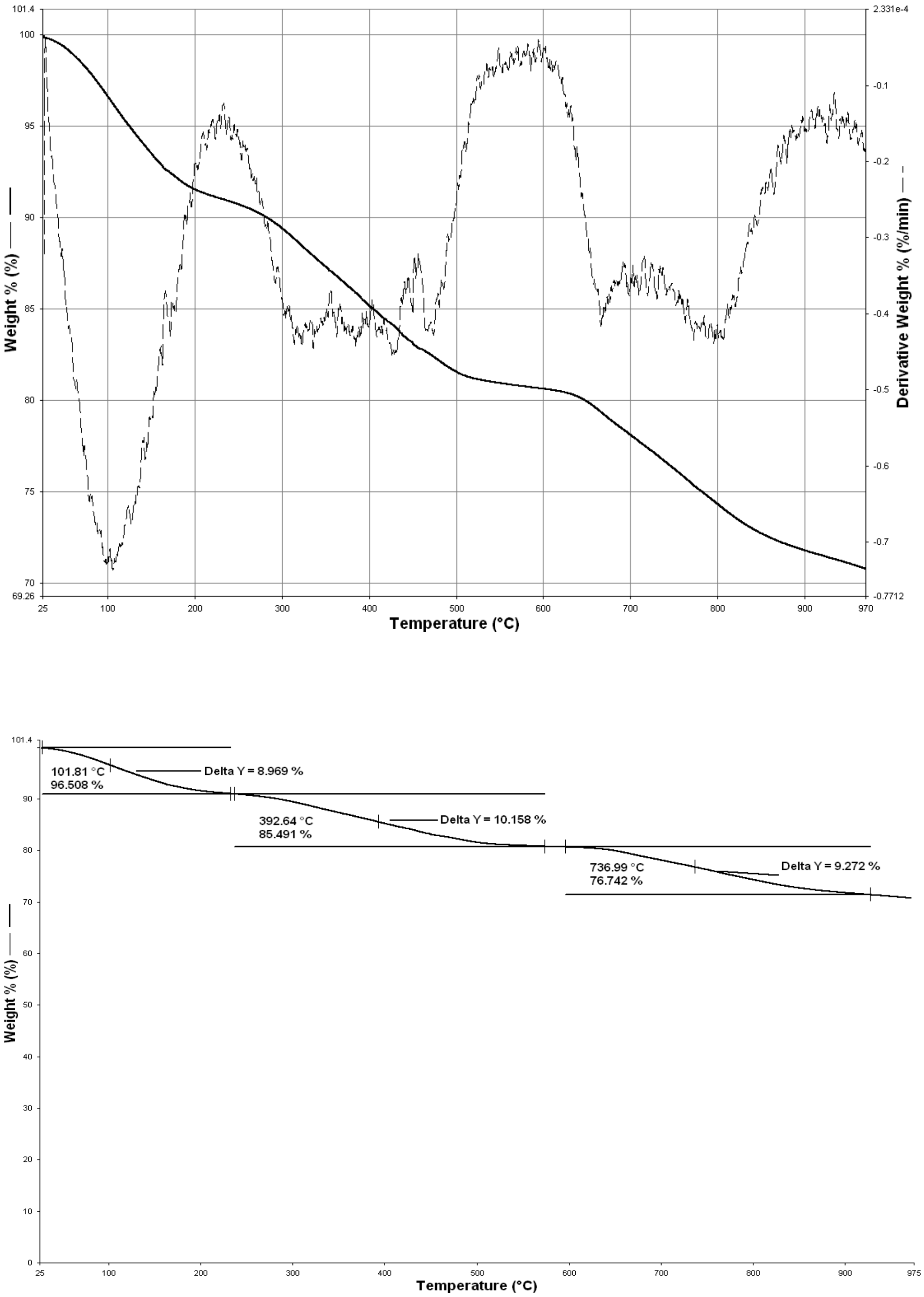


Figure D.2 TGA Thermogram for in-oven annealed PBI/Zeolite-3A membrane

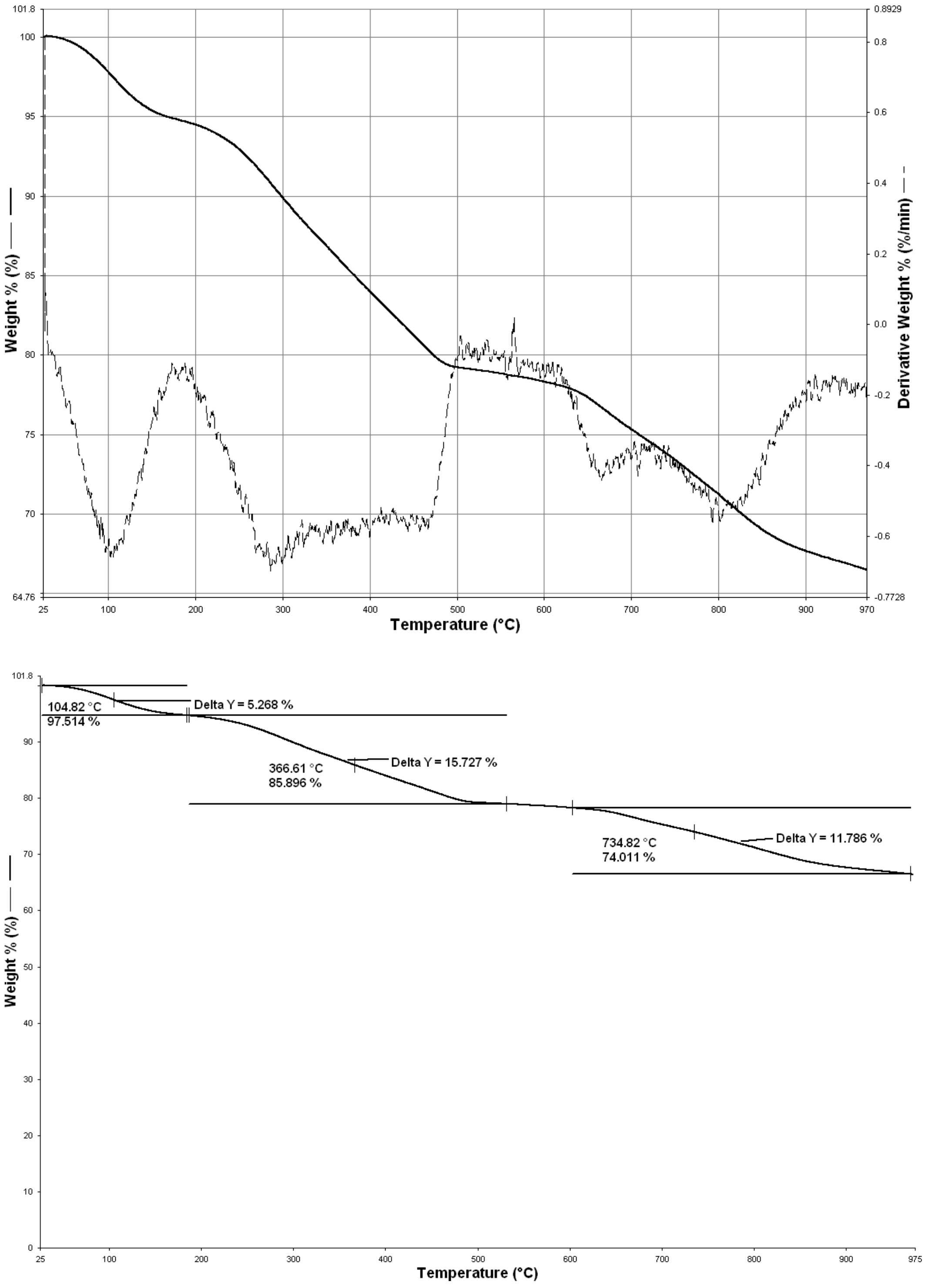


Figure D.3: TGA Thermogram for in-line annealed neat PBI membrane

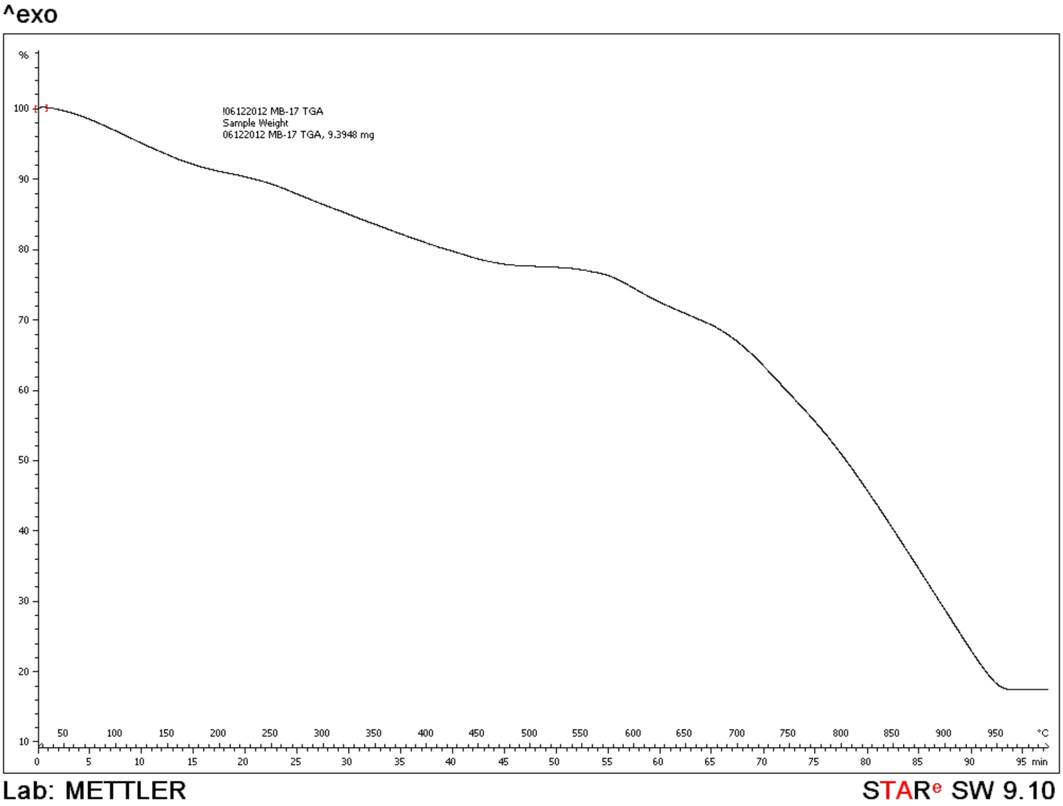
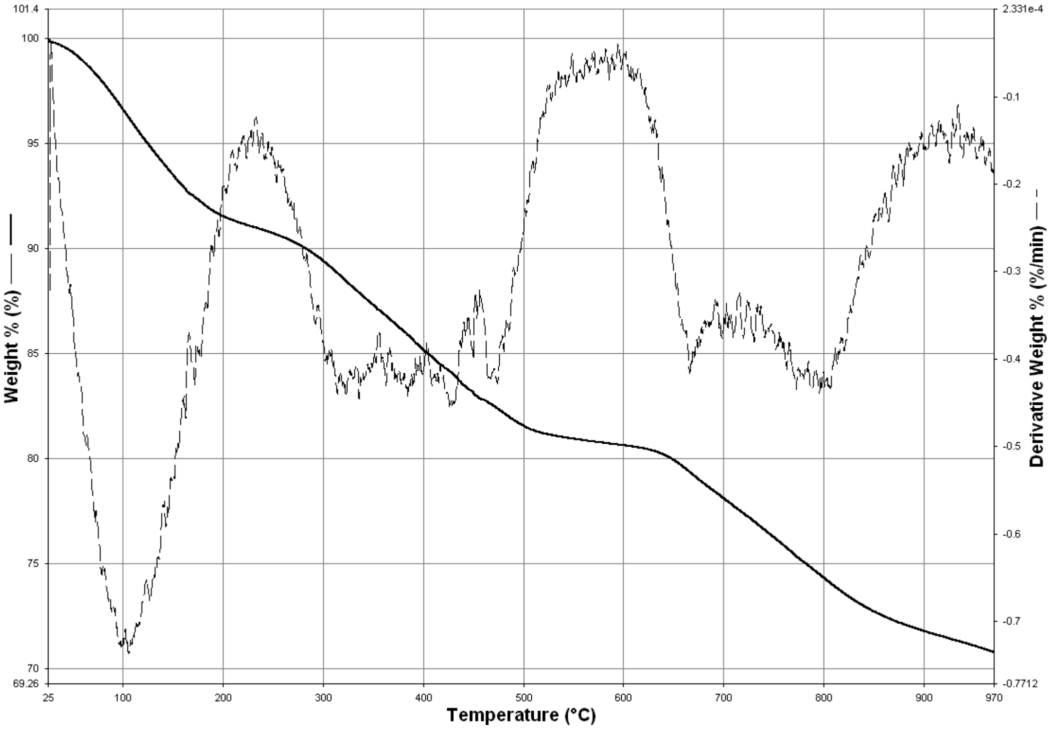


Figure D.4: TGA Thermogram for in-line annealed neat PBI/Zeolite 3A membrane



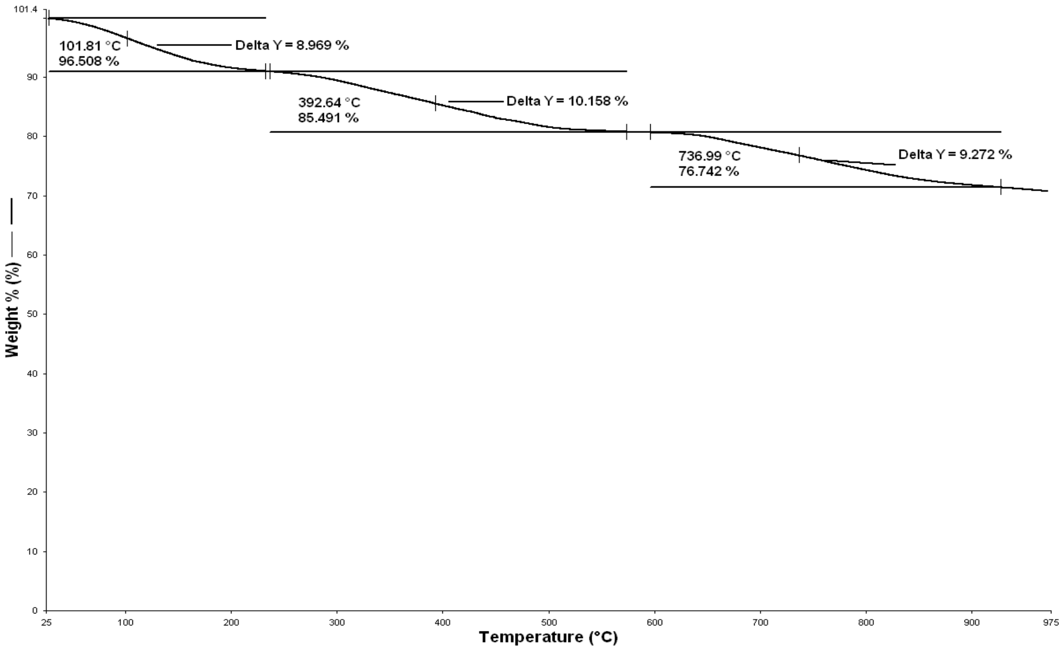
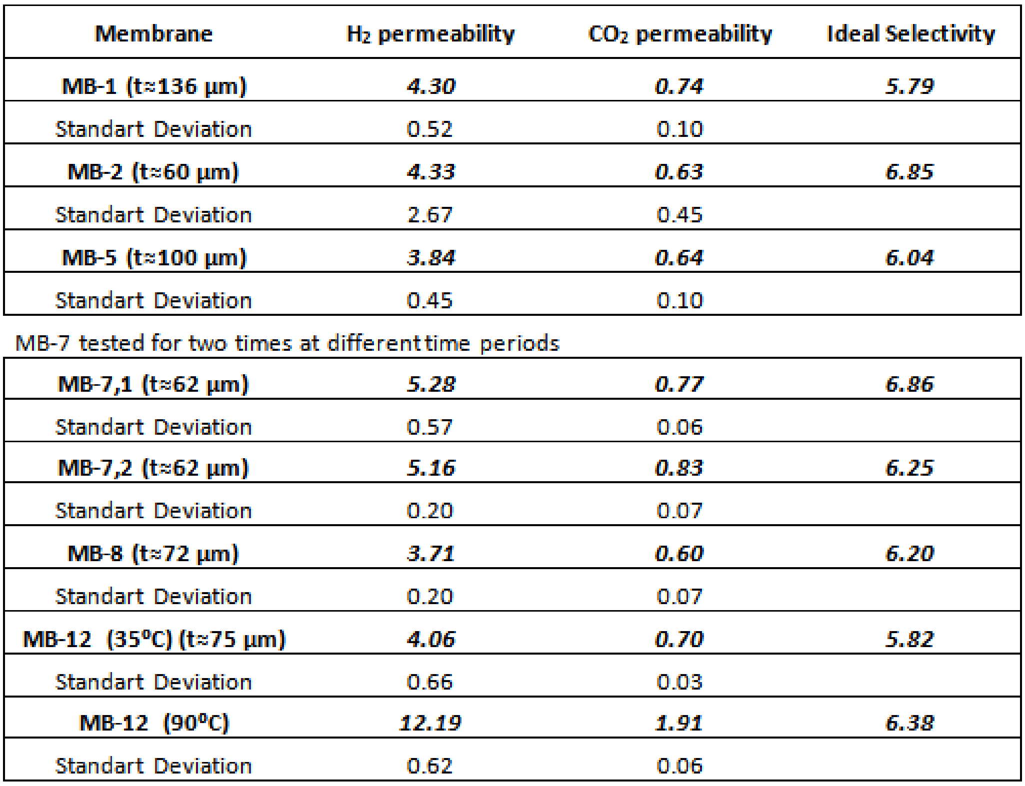


Figure D.5: TGA Thermogram for in-line annealed neat PBI/SAPO-34 membrane

APPENDIX E

PERMEABILITY AND SELECTIVITY DATA OF TESTED MEMBRANES

Table E.1 Single gas permeabilities of in-oven annealed neat PBI membranes



Membrane	H_2 permeability	CO_2 permeability	Ideal Selectivity
MB-1 (t≈136 µm)	***4.30***	***0.74***	***5.79***
Standart Deviation	0.52	0.10	
MB-2 (t≈60 µm)	***4.33***	***0.63***	***6.85***
Standart Deviation	2.67	0.45	
MB-5 (t≈100 µm)	***3.84***	***0.64***	***6.04***
Standart Deviation	0.45	0.10	

MB-7 tested for two times at different time periods

MB-7,1 (t≈62 µm)	***5.28***	***0.77***	***6.86***
Standart Deviation	0.57	0.06	
MB-7,2 (t≈62 µm)	***5.16***	***0.83***	***6.25***
Standart Deviation	0.20	0.07	
MB-8 (t≈72 µm)	***3.71***	***0.60***	***6.20***
Standart Deviation	0.20	0.07	
MB-12 (35°C) (t≈75 µm)	***4.06***	***0.70***	***5.82***
Standart Deviation	0.66	0.03	
MB-12 (90°C)	***12.19***	***1.91***	***6.38***
Standart Deviation	0.62	0.06	

Table E.2 Single gas permeabilities of in-line annealed neat PBI membranes

(Membranes= 2w/v% PBI)

Membrane	**T,C**	**H_2 permeability**	**CO_2 permeability**	**Ideal Selectivity**
MB-11 (t≈75 µm)	35	***7.77***	***3.37***	***2.31***
Standart Deviation		0.16	0.04	
	50	***9.94***	***4.25***	***2.34***
Standart Deviation		0.08	0.03	
	70	***15.24***	***6.31***	***2.42***
Standart Deviation		0.65	0.67	
	90	***22.64***	***9.07***	***2.50***
Standart Deviation		1.99	0.03	
MB-13 (t≈75 µm)	35	***7.31***	***3.17***	***2.31***
Standart Deviation		0.27	0.10	
	50	***9.75***	***3.81***	***2.56***
Standart Deviation		0.38	0.02	
	70	***15.78***	***5.79***	***2.73***
Standart Deviation		0.12	0.11	
	90	***21.98***	***8.52***	***2.58***
Standart Deviation		0.81	0.09	
MB-14 (t≈85 µm)	35	***7.64***	***3.31***	***2.31***
Standart Deviation		0.11	0.05	
	50	***10.85***	***4.24***	***2.56***
Standart Deviation		0.20	0.02	
	70	***15.57***	***5.97***	***2.61***
Standart Deviation		0.16	0.10	
	90	***22.52***	***8.34***	***2.70***
Standart Deviation		0.33	0.13	

Table E.3 Single gas permeabilities of mixed matrix membranes

Membrane	Filler Amount	Annealing Type	T (°C)	H_2 permeability	CO_2 permeability	Ideal Selectivity
MB-4 (t≈75 µm)	**25w/w% Zeolite 3A**	**In-oven**	35	***5.47***	***0.99***	***5.53***
Standart Deviation				0.25	0.03	
MB-6 (t≈80 µm)	**25w/w% Zeolite 3A**	**In-oven**	90	***3.92***	***0.78***	***5.00***
Standart Deviation				0.22	0.03	
MB-16 (t≈85 µm)	**20 w/w% SAPO-34**	**In-line**	35	***8.01***	***2.80***	***2.86***
Standart Deviation				0.20	0.08	
			50	***9.95***	***3.40***	***2.93***
Standart Deviation				0.07	0.41	
			70	***17.37***	***5.85***	***2.97***
Standart Deviation				0.16	0.06	
			90	***26.73***	***8.74***	***3.06***
Standart Deviation				0.13	0.09	
MB-17 (t≈90 µm)	**25 w/w% Zeolite 3A**	**In-line**	35	***7.69***	***2.92***	***2.63***
Standart Deviation				0.11	0.16	
			50	***11.81***	***4.30***	***2.75***
Standart Deviation				0.30	0.05	
			70	***17.59***	***6.26***	***2.81***
Standart Deviation				0.20	0.04	
			90	***26.54***	***9.10***	***2.92***
Standart Deviation				0.27	0.15	

APPENDIX F

DMAc BOILING POINT WITH RESPECT TO PRESSURE

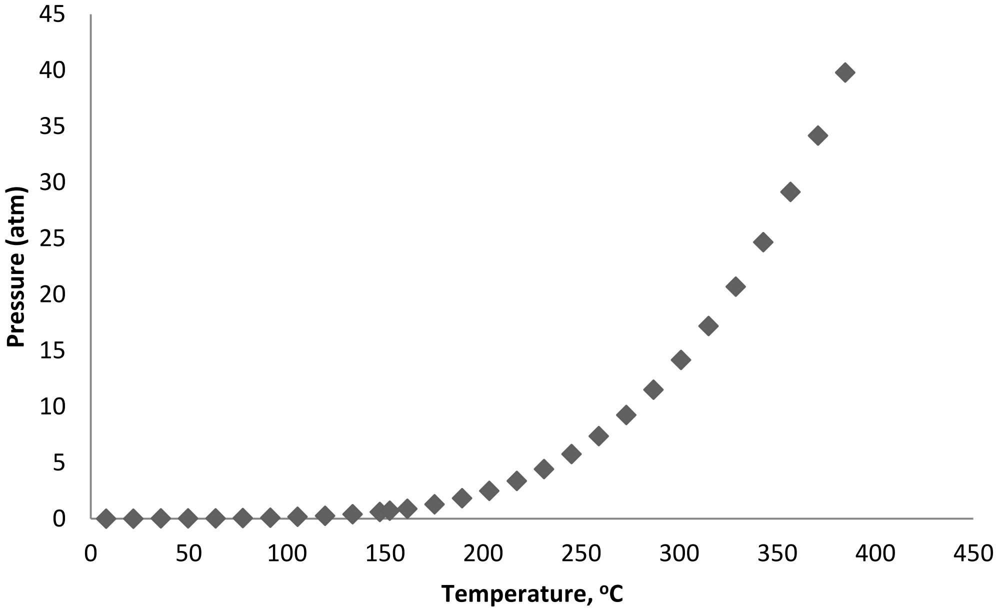


Figure F.1: DMAc boiling point vs. pressure diagram