EFFECT OF COMPATIBILIZERS ON THE GAS SEPARATION PERFORMANCE OF POLYCARBONATE MEMBRANES

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ABSTRACT

EFFECT OF COMPATIBILIZERS ON THE GAS SEPARATION PERFORMANCE OF POLYCARBONATE MEMBRANES

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In this study, the effect of compatibilizers on the gas separation performance of polycarbonate (PC) membranes was investigated. Membranes were prepared by solvent evaporation method. They were characterized by single gas permeability measurements of O_2, N_2, H_2 and CO_2 as well as scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and Fourier transform infrared spectrometry (FTIR).

Membranes containing 0.5 to 10 w% p-nitroaniline (pNA) were prepared to study the effect of compatibilizer concentration on the membrane performance. Permeabilities of all gases decreased but selectivities increased with pNA concentration. The membranes with 5 w% pNA showed a selectivity of 114.5 for H_2 over N_2, 53.9 for CO_2 over N_2 and 13.4 for O_2 over N_2 at room temperature, whereas, the H_2/N_2, CO_2/N_2 and O_2/N_2 selectivities for pure PC membranes were 43.5, 20.6 and 5.6, respectively. The N_2 permeabilities through pure PC membrane and 5 w% pNA/PC membrane were 0.265 and 0.064 barrer, respectively.

The glass transition temperature of the membranes decreased with increasing pNA concentration. FTIR spectra showed that the peaks assigned to nitro and amine groups of pNA shifted and/or broadened. The DSC and FTIR results suggested an interaction between PC and pNA.

The effect of type of compatibilizer was also studied. The compatibilizers were 4-amino 3-nitro phenol (ANP), Catechol and 2-hydroxy 5-methyl aniline (HMA). Similar to membranes prepared with pNA, membranes prepared with these compatibilizers had a lower permeability and glass transition temperature but higher selectivity than pure PC membranes. Their FTIR spectra were also indicated a possible interaction between PC and compatibilizer.

In conclusion, PC/compatibilizer blend membranes for successful gas separation were prepared. Low molecular weight compounds with multifunctional groups were found to effect membrane properties at low concentration range, 0.5-5 w%.

Keywords: Gas Separation, Polycarbonate membrane, Compatibilizer, Antiplasticization, p-nitroaniline.

ÖZ

UYUMLAŞTIRICILARIN POLİKARBONAT MEMBRANLARIN GAZ AYIRIM PERFORMANSINA ETKİSİ

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Bu çalışmada, uyumlaştırıcıların polikarbonat (PC) membranlarının gaz ayırım performansına etkisi incelenmiştir. Membranlar çözücü buharlaştırma yöntemiyle hazırlanmıştır. Membranların, O_2, N_2, H_2 ve CO_2 gazları ile tek gaz geçirgenlik ölçümleri, tarama elektron mikroskobu (SEM), fark taramalı kalorimetre (DSC) ve Fourier çevrimli kızılötesi spektrofotometre (FTIR) ile karekterizasyonu çalışılmıştır.

Yüzde (ağırlıkça) 0.5-10 p-nitroanilin (pNA) içeren membranlar hazırlanarak pNA derişiminin membran performansı üzerine etkisi incelenmiştir. pNA derişimi arttıkça gazların geçirgenliklerinin azaldığı, seçiciliklerinin arttığı gözlenmiştir. Saf PC membranın göstermiş olduğu H_2/N_2, CO_2/N_2 ve O_2/N_2 seçicilikleri sırasıyla 43.5, 20.6 ve 5.6 iken % (ağırlıkça) 5 pNA içeren membranlarda 114.5, 53.9 ve 13.4'e yükselmiştir. Saf PC membranların azot geçirgenliği % (ağırlıkça) 5 pNA katılmasıyla 0.265 barrer' den 0.064 barrer' e azalmıştır.

Membranların camsı geçiş sıcaklıkları artan pNA derişimiyle azalmıştır. FTIR spektrumlarında pNA' nin nitro ve amin gruplarına ait tepe noktalarında kayma ve yayılma gözlenmiştir. DSC ve FTIR sonuçları PC ile pNA arasında bir etkileşimin olabileceğini göstermiştir.

Ayrıca uyumlaştırıcı türlerinin etkisi çalışılmıştır. Bu amaçla 4-amino 3-nitro fenol (ANP), Katekol ve 2-hidroksi 5-metil anilin (HMA) uyumlaştırıcı olarak denenmiştir. Bu uyumlaştırıcılarla da pNA'e benzer şekilde geçirgenliklerin ve camsı geçiş sıcaklıklarının azaldığı seçiciliklerin ise arttığı gözlenmiştir. Ayrıca FTIR spektrumları PC ile uyumlaştırıcı arasında olası bir etkileşimi göstermektedir.

Sonuç olarak, PC/uyumlaştırıcı gaz ayırım membranları başarıyla hazırlanmıştır. İşlevsel grupları çok, molekül ağırlığı düşük olan bileşiklerin, çok küçük derişim aralığında, % (ağırlıkça) 0.5-5, membran özelliklerini etkileyebilecekleri bulunmuştur.

Anahtar sözcükler: Gaz ayırımı, Polikarbonat membran, Antiplastizasyon, Uyumlaştırıcı, p-nitroanilin.

To my father, Ersin Şen and
my mother Yurdagül Şen

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NOMENCLATURE

A :Membrane area

dn/dt :Molar flow rate

dp/dt :Pressure increase
J :Flux
K :Adjustable parameter
M :Molecular weight of gas
P :Permeability
p_f :Feed side pressure
p_p :Permeate side pressure
R :Ideal gas constant
T :Temperature
T_g :Glass transition temperature
V_d :Dead volume
w_d :Weight fraction of additive
w_p :Weight fraction of polymer

Greek Letters
α :Selectivity
ν :Volumetric flow rate
ρ :Density of the permeate gas
δ :Membrane thickness

Abbreviations:
ANP :4-amino 3-nitro phenol
AHMP :2-amino 4-hydroxy 6-methyl pyrimidine
CMS :Carbon molecular sieve
DCM :Dichloromethane

DSC :Differential Scanning Calorimeter
FTIR :Fourier transform infrared
HMA :2-hydroxy 5-methyl aniline
LMWC :Low molecular weight compound
MMM :Mixed matrix membrane
PC :Polycarbonate
PI :Polyimide
pNA :para-nitroaniline
SEM :Scanning electron microscopy
TAP :2,4,6-triaminopyrimidine
TGA :Thermal gravimetric analysis

CHAPTER 1

INTRODUCTION

Membrane based separation has become an important process in the chemical industry in the last twenty-five years [1]. The advantages of membrane gas separation technology compared to its competitors like cryogenic separations, pressure swing adsorption, are:

- low energy requirement,
- adjustable membrane properties,
- separation under low pressure and temperature,
- easy combination with other separation processes,
- easy to scale-up.

Membranes are selective barrier films between two phases and allow the preferential transport of certain molecules under the influence of a gradient in pressure [1]. The physical and chemical properties of both the membrane material and the permeating components determine the membrane performance. The performance of a membrane is determined by two parameters; selectivity of the membrane to a component over another and permeability through the membrane.

For gas separation membranes, permeability is the rate at which a permeate passes through a membrane and is expressed as,

$$P = J\,\delta / (p_f - p_p)$$

where J is flux of gas through the membrane, p_f and p_p are the partial pressures of the gas on the feed and permeate side, respectively; and δ is the thickness of the membrane. The ideal selectivity, α_{AB}, that is the ratio of permeabilities of single gases, is defined by the relation,

$$\alpha_{AB} = P_A / P_B$$

Membranes can be classified according to their material of construction, morphology and structure. Polymers providing a broad range of properties are very common membrane materials. They exhibit a good separation performance for many gas and liquid mixtures [2-7]. They can be easily processed into membranes and easily implemented into the membrane modules because of their flexibility. Non-porous polymers are usually applied in gas separation. Cellulose acetates, polysulfones, polycarbonates and polyimides are the most important ones for gas separation membranes [2].

The structure and morphology of polymer membranes also influences membrane performance. Three types of structures are generally found in membranes: symmetric, asymmetric and composite (Figure 1.1),[2]. Symmetrical membranes consist of a single polymer layer. They can be porous or non-porous (dense, homogenous). Asymmetric membranes are made up of a thin dense skin layer with a porous support layer underneath. Separation is generally controlled by the dense surface layer. Composite membranes are special type of an asymmetric membrane in which the top layer and sublayer originate from different materials. Properties of each layer can be separately optimized for the highest gas separation performance.

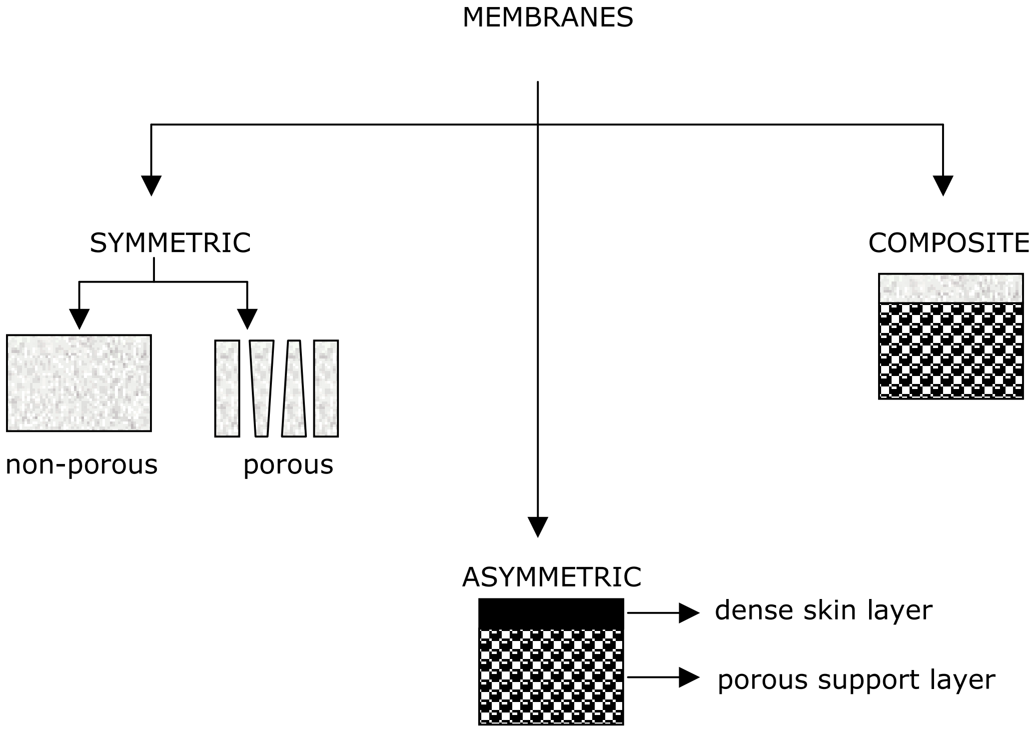


Figure 1.1 Classification of membranes according to their structure

The latest emerging membrane morphology is mixed matrix membrane, which is composed of two interpenetrating matrices of different materials as shown in Figure 1.2 [9].

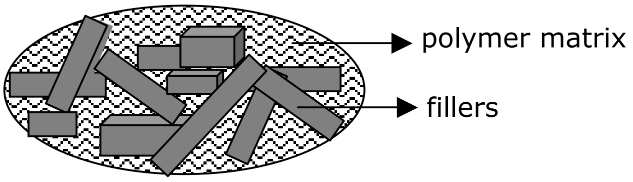


Figure 1.2 Mixed matrix membrane structure

In mixed matrix membranes, (MMM), the continuous phase can be a rubbery or glassy polymer, and the dispersed phase are usually fillers, such as zeolites and carbon molecular sieves, (CMSs) [8-10]. These fillers may provide higher selectivity to membranes due to their well defined pore size, high surface area and shape selective property. Therefore, MMMs have potential to combine the easy processability of polymers with the superior gas separation properties of fillers and to increase the separation performance of polymeric membranes.

The biggest difficulty on the preparation of MMMs is to obtain membrane without voids. Glassy polymers interact weakly with the zeolitic framework and can result in a series of non-selective voids surrounding the zeolite particles [9, 11, 12]. These voids may connect to each other in the matrix and provide an alternative path for penetrating molecules, which decreases the separation performance of membrane.

A number of methods have been investigated to solve this problem, such as modification of the external surface zeolite crystals by silylation [13], preparation of membranes above the glass transition temperature [13] and use of compatibilizers [14]. Compatibilizers are low molecular weight materials which interact both with the zeolite and the polymer. It is expected that these materials may eliminate the interfacial voids and improve the performance of MMMs.

In this study, the effect of compatibilizer type and concentration on the performance of polycarbonate gas separation membranes was investigated. Different low molecular weight compounds, which may interact with both the polymer and zeolite particle were selected as compatibilizers. Dense homogenous polycarbonate membranes without a zeolite were prepared to see the effect of compatibilizer on the matrix polymer. The performance of the membranes were determined by single gas permeation measurements. The membranes were also characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and Fourier transform infrared spectrometer (FTIR).

CHAPTER 2

LITERATURE SURVEY

The performance of a polymeric membrane is determined by permeability and selectivity. A considerable amount of information has been available for many years on permeabilities and selectivities of large variety of polymers to different gases. Polymers that are more permeable are generally less selective and the polymers that are more selective are less permeable [5]. The balance between the permeability and selectivity was presented in a well-known trade off curve by plotting performance data of the polymeric membranes, Figure 2.1 [3].

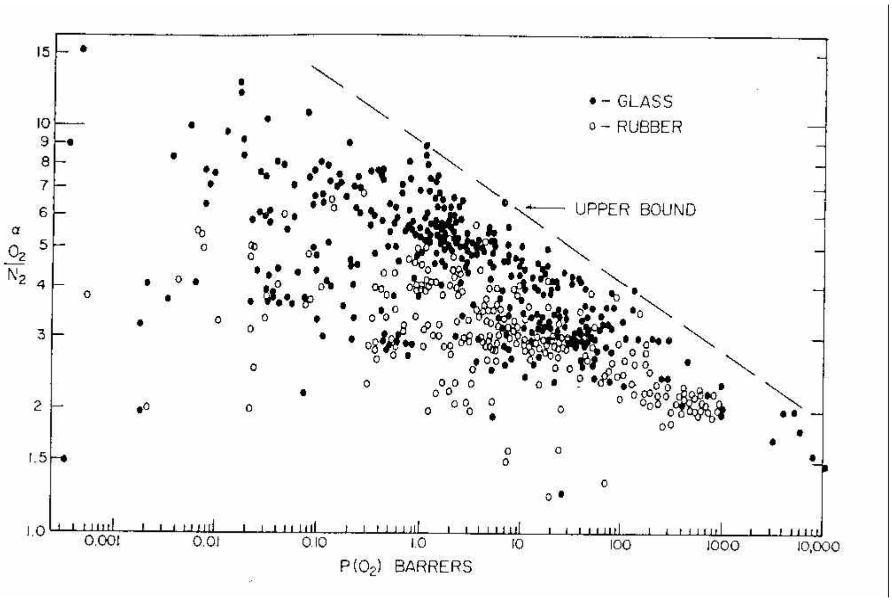


Figure 2.1 Upper bound trade off curve (Robeson plot) for O_2/N_2 selectivity versus O_2 permeability

This figure presents O_2/N_2 selectivity versus oxygen permeability for many polymers on log-log scale. The same trade off curve was drawn for different gas pairs like H_2/N_2, CO_2/CH_4. Materials with the best performance would be in the upper right hand corner of this figure. However, materials with permeability/selectivity combinations above and to the right of the line drawn in this figure are exceptionally rare. This line defines the so called upper-bound combinations of permeability and selectivity of known polymer membrane materials for this particular gas pair [3, 5].

The upper bound performance characteristics were described by the following equation [5] :

$$\alpha_{A/B} = \beta_{A/B} / P_A{}^{\lambda AB}$$

P_A is the permeability, $\alpha_{A/B}$ is selectivity. λ_{AB} is an emprical parameters depends on gas size, $\beta_{A/B}$ is also an empirical parameter depends on both λ_{AB} and gas solubility in polymer. According to Freeman [5] λ_{AB} can not be changed with polymer development but $\beta_{A/B}$ can be adjusted by polymer structure manipulation. This implies that upper bound line can not be exceeded by changing the chemical structure of classical polymers.

In recent studies addition of molecular sieve materials such as zeolite and carbon molecular sieves (CMSs) into polymer matrix has been shown as an unconventional way to exceed the upper bound curve [8-10]. These additives lie well above the upper bound line. Combining this property of these materials with easy processability of polymers may increase the separation performance of polymeric membranes. This is the origin of mixed matrix membrane idea.

Another alternative to increase the gas separation performance of polymeric membranes is blending polymers with low molecular weight compounds (LMWCs). The incorporation of LMWCs, like naphtylamine, phthalates and fluorenes, into glassy polymers (polysulfones, polyimide) reduce permeability of the membranes, but increase their selectivity and may result in better separation performances [15,16].

2.1 Mixed Matrix Membranes

The incorporation of zeolites into rubbery or glassy polymers have been shown to enhance the gas separation performances of the conventionally employed polymeric membranes. These are called mixed matrix membranes (MMMs).

Zeolite-filled rubbery polymer membranes were investigated by Hennepe et al. for pervaporation and gas separation purposes [17, 18]. Results showed that addition of zeolites silicalite-1, NaX and AgX to polydimethylsiloxane, increased both permeability and selectivity of the membranes. They modelled the transport through zeolite filled membranes and claimed that the increase in selectivity resulted from a longer pathway for the slowest component around the zeolite particle. The increase in permeability was explained by an increase in sorption of the components in the membrane.

Jia et al. [19] was also studied with silicalite-1 filled polydimethylsiloxane membranes. The permeability of He, H_2, O_2 and CO_2 was observed to increase, while that of N_2, CH_4 and C_4H_{10} was observed to decrease. They concluded that silicalite played the role of a molecular sieve, facilitated the permeation of smaller molecules but hindered that of larger molecules. Selectivity of O_2/N_2 increased from 2.1 to 2.5, 2.7, 2.9 for 50, 64, 70 w% silicalite, respectively.

Duval et al. [20] examined an array of both zeolites and commerciall carbon molecular sieves for a range of rubbery polymers. They observed significant improvement in CO_2/CH_4 selectivity from 13.5 to 35 for a MMM prepared with nitrile-butadiene rubber and 46 vol.% zeolite KY. They also reported slight enhancement for O_2/N_2 selectivity, such as from 3.0 to 4.7 for an ethylene-propylene rubber MMM with 53 vol.% silicalite. However, they showed that MMM prepared from CMSs demonstrated no improvement attributed to the dead end porous nature of CMS.

These studies performed with MMMs, which used elastomeric or rubbery polymers as the continuous matrix phase, indicated that performance results are not of practical importance compared to available pure glassy polymers. For example, polyimide is a glassy polymer and it has higher separation performance than the MMMs with rubbery polymers. Its O_2/N_2 selectivity is 7.2 [8, 11]. Subsequently, zeolite filled glassy polymer membranes were investigated. Gürkan et al. [21] focused on the separation of O_2/N_2 and H_2/N_2 gas pairs using a zeolite 13X filled polysulfone membrane made by extrusion. They found substantial increases in selectivities when compared with pure polysulfone.

Süer et al. [22] indicated the importance of the resultant heterogenous morphology of MMMs and the importance of preparation and pretreatment factors which may affect the structure and performance of MMMs. A MMM of polyethersulfone and zeolite 13X or 4A were developed and the permeation rates of N_2, O_2, Ar, CO_2 and H_2 were measured. The morphology of heterogenous membranes was investigated by SEM. It was concluded that both permeabilities and selectivities were increased at high zeolite loading (42-50 w%). It was demonstrated that the addition of zeolites induced a microporous cavity and channeling system which was probably the result of partial incompatibility between polymer and zeolite. Changes in membrane performance were affected by zeolite type, its amount in the matrix and the resultant micromorphology of the membranes. Considered micromorphology includes presence of zeolite particle aggregation and cave-like voids created around the zeolitic fillers.

Battal et al. [23] then focused on the dependence of permeabilities and selectivities on feed composition and applied binary gas permeability measurements with the same MMM studied previously. A mechanism for transport pathways of gas through the MMM was also proposed.

As an alternate approach to the zeolite filled polymeric membranes, Gülşen and Hacarlıoğlu [24, 25] used a conducting polymer, polypyrrole (PPy) as filler in polybisphenol-A-carbonate (PC) membranes, which is an insulating polymer. One of their objectives was to solve the incompatibility problem of zeolite filled membranes by using similar materials in membrane preparation. The effects of PC content of membrane, annealing and solvent evaporation temperature, supporting electrolyte type and its concentration on the membrane performance were investigated. The results showed that PPy filled PC MMMs has selectivities higher than pure PC membrane. Hacarlıoğlu [24] also studied the effect of membrane preparation parameters on the gas separation performance of pure PC membranes. She showed that the performance of the membranes strongly depends on the type of solvent and concentration. The membranes that were cast from a solution of chloroform exhibited higher permeabilities and selectivities than the ones which were cast from a solution of dichloromethane. However, when chloroform was used as solvent, the permeabilities showed a decrease with increasing PC composition while the performances of the membranes casted from dichloromethane permeabilities were slightly affected from the composition change. She claimed that the solvents which have higher boiling point and higher molar volume resulted in higher permeabilities in membranes.

The separation performance of zeolite/glassy polymer mixed matrix membranes may be improved by eliminating non-selective voids surrounding the zeolite particles that emerge due to poor adhesion between the polymer matrix and the zeolite particle.

Duval et al. [13] proposed two methods to make the zeolite surface more compatible with the polymers. In the first method, the external surface of zeolite crystals was modified by silane coupling agents that consecutively link to the polymer chain. In the second method, the solvent used to prepare the polymer solution was evaporated above the glass transition temperature of the polymer during membrane formation. Silicalite-1 was used as zeolite filler and glassy polymers such as cellulose acetate, polysulfone, polyetherimide and polyimide were used as polymer phase. Although they observed improved polymer-zeolite contact with SEM micrographs, selectivities for CO_2/CH_4 decreased or remained unchanged. For example, for polyetherimide 50 w% silicalite-1 addition decreased its CO_2/CH_4 selectivity from 61 to 34. In a similar study silane coupling agent, aminopropyl silane was used to improve zeolite surface adhesion to the polymer matrix [12]. It was observed that while this modification led to improved adhesion, separation performance was worse than the results obtained with unmodified zeolite.

Mahajan et al. [26] identified important parameters for MMM formation with glassy polymers. They emphasized the importance of appropriate selection of polymer matrix and zeolite phases and suggested that the polymer matrix must have sufficient permeability for gas molecules to have continuous pathways through the zeolites. Based on these criteria, Zimmerman et al. [8] used Matrimid® polyimide and zeolite 4A (20 vol.%) for O_2/N_2 separation, although permeability increased from 1.32 to 4.00 barrer, selectivity remained at

Matrimids original value of 7.2. This result indicated that proper material selection, while necessary, was not sufficient due to transport through the voids.

In another study, a different strategy was used to improve polymer-zeolite contact. Mahajan et al. [11] added a plasticizer to decrease the glass transition temperature, T_g, of polymer for obtaining flexible membranes. They claimed that maintaining flexibility during membrane formation may lead to good adhesion between the polymer and zeolite. Di-butyl phthalate (DBP), 4-hydroxy benzophenone (HBP) was used as a plasticizer with a plasticizer/Matrimid ratio of 25/75 (w/w). The O_2/N_2 selectivity decreased from 7.2 to 6.6 and 6.4 for DBP and HBP, respectively while O_2 permeability changed from 1.32 to 1.5 barrer for DBP and to 0.55 barrer for HBP.

The studies mentioned above could not show any clear explanation why zeolite filled glassy polymer membranes could not improve separation performance in desired level. It was considered that voids still remained after surface modification of zeolite by silane coupling agents, membrane preparation above T_g of polymer, proper material selection and plasticizer addition.

An alternative way to eliminate the voids is to use of a compatibilizer. A compatibilizer is a chemical linkage which improve the adhesion between the polymer and zeolite.

Yong et al. [14] introduced an organic compound 2,4,6-triaminopyrimidine (TAP), as a compatibilizer to eliminate interfacial voids between polyimide (PI) chains and zeolite particles. They suggested that this low molecular weight compound (LMWC) could interact simultaneously with zeolites and polymers and interfacial voids could be eliminated. Their permeability and selectivity results were shown in Table 2.1.

Table 2.1 Permeability and selectivity results of PI/TAP membranes [14]

Membrane	Permeability (barrer)				Selectivity	
	CO_2	CH_4	O_2	N_2	CO_2/N_2	O_2/N_2
[1]PI	8.34	6.86	1.50	0.218	38.3	6.88
[2]PI/TAP (1/0.21w/w)	0.194	0.0023	0.0346	0.00224	86.6	15.4
[3]PI/4A (1/0.43 w/w)	9.36	4.19	1.91	0.455	20.6	4.2
PI/4A/TAP (1/0.43/0.21 w/w/w)	0.185	0.0003	0.033	0.00181	102	18.2

[1] PI: polyimide, [2] TAP: 2,4,6-triaminopyrimidine, [3] 4A: zeolite 4A

According to their results, PI/TAP membranes showed lower permeability but higher selectivity than pure PI membranes, which was explained with the formation of hydrogen bond between PI and TAP. On the other hand, PI/zeolite 4A membranes showed higher permeability but lower selectivity than pure PI membrane. They suggested that these were resulted from the interfacial void formation between zeolite particles and PI matrix. They observed that PI/zeolite 4A/TAP membrane showed lower permeability but higher selectivity for all gases than the PI/TAP matrix. The PI/zeolite 4A/TAP membrane showed a selectivity of 617 for CO_2/CH_4 which was located over the upper bound line.

Yong et al. claimed that LMWCs with multifunctional groups capable of making interactions with the glassy polymer chain and zeolite particles eliminate the interfacial voids and increase the separation performance of the membrane.

PI/TAP and PI/4A/TAP membranes had similar separation performances (Table 2.1), therefore, the main effect in increase in performance might come from the TAP. TAP concentration in the membrane matrix was high and it acted as a main component of the membrane, not as additive.

2.2 Polymer / LMWC Blend Membranes

The addition of certain types of low molecular weight compounds into glassy polymers causes an increase in stiffness because of the reduced rates of segmental motions in the polymer chain. This phenomenon is known as antiplasticization and the LMWCs which cause this phenomenon are known as antiplasticizers in the polymer literature [27-30]. In the membrane area, this antiplasticization effect has been shown to appear by a decrease in the permeability of gases and by generally an increase in the selectivity [15, 16].

Robeson [31] showed that the carbon dioxide permeability of polysulfone antiplasticized with 10 w% 4,4′-dichlorodiphenylsulfone (DDS) decreased. The permeability value of CO_2 decreased from 5.76 to 2.16 with the addition of DDS. He suggested that DDS filled the free volume of polymer and reduced permeability.

The effect of various antiplasticizers on the gas permeability of polysulfone (PSF) and poly(phenylene oxide), (PPO), membranes were studied in detail by Maeda and Paul [32, 33]. As antiplasticizers 4,4′-dichlorodiphenyl sulfone, N-phenyl-2-naphtylamine, tricreysl phosphate and different type of sebacates were added into polymers in the concentration range of 10-30 w%. It was shown that these compounds reduced the permeabilities of all gases studied, He, CO_2 and CH_4 and increased the selectivities of He/CH_4, He/CO_2 and CO_2/CH_4 gas pairs. They also measured glass transition temperatures of these blends and observed a significant decrease in glass transition temperatures. For PSF this reduction was from 185 °C to 50 °C with the addition of 30 w% antiplasticizer. They claimed that there was a relation between reduction in T_g and antiplasticization effect.

Ruiz-Treviňo and Paul [15] examined the effect of various naphthalene-, bisphenol-, and fluorene-, based additives on performance properties of the membranes with bisphenol A polysulfone (PSF). They concluded that these additives increased selectivity and reduced permeability of PSF membrane when incorporated at the concentration range of 10-30 w%. They speculated that the compounds which have hydroxyl groups and polar atoms in their structure showed interactions with PSF and this led to reduction in free volume by bringing the polymer chains closer. They calculated glass transition temperatures of the membranes by weighted average of additives and polymer with an adjustable parameter. They came to a conclusion that T_g of membrane decreased due to low T_g of the additives.

Above studies have shown that the physical incorporation of low molecular weight compounds into glassy polymers generally reduce their permeability to gases but increase their selectivity for certain gas pairs. In these studies these LMWCs were used to obtain their antiplasticization effect on the polymer. These antiplasticizers were relatively large molecules in a molecular weight range of 166-466 and they were used in high concentrations, 10-30 w%.

However, similar type of LMWCs were used to increase the flexibility of the polymer by reducing its T_g. This phenomenon was used in formation of void free MMMs. Di-butyl phthalate and 4-hydroxy benzophenone were examples of these compounds which were used for this purposes. Their concentration was 33 w% in the membrane [11].

In addition LMWCs were also used as compatibilizer to eliminate the interfacial voids in MMMs by filling the space between the zeolite particles and polymer chains [14]. 2,4,6-triaminopyrimidine was used as a compatibilizer with a concentration of 21 w% in a study. All different type of applications of this LMWCs were presented in Table 2.2.

Table 2.2 Comparison of LMWCs added polymeric membranes

Ref.	LMWC*	Function of LMWC	LMWC w/w %	Polymer**	P (barrer)		α
					N_2	O_2	O_2/N_2
Yong et al. [14]	TAP	compatibilizer	21	PI	0.218	1.50	6.88
				PI/TAP	0.0022	0.0346	15.40
Mahajan et al. [11]	DBP	plasticizer	33	PI	0.183	1.32	7.20
	HBP			PI/DBP	0.227	1.50	6.60
				PI/HBP	0.086	0.55	6.40
Paul et al. [15]				PSF	0.248	1.39	5.60
	N-PNA	antiplasticizer	20	PSF/N-PNA	0.016	0.13	8.13
	Fluorene			PSF/fluorene	0.048	0.33	6.88
	TMBPA			PSF/TMBPA	0.024	0.18	7.50
Larocca et al. [57]				PEI		0.60	
	N-PNA		23	PEI/N-PNA		0.15	
	TBBPA	antiplasticizer	32	PEI/TBBPA		0.16	
	BHT		23	PEI/BHT		0.32	

*TAP: 2,4,6-triaminopyrimidine, DBP: Di-butyl phthalate, HBP: 4-hydroxy benzophenone, N-PNA: N-phenyl-2-naphtylamine, TMBPA: tetramethylbisphenol A, TBBPA: 4,4′-Isopropylidene 2,6-di-bromophenol, BHT: 2,6-di-tert-butil p-cresol.

**PI: Polyimide, PSF: Polysulfone, PEI: Polyetherimide.

Since above mentioned studies showed that added LMWCs strongly effect molecular properties and membrane performances of glassy polymers, the effect of LMWCs, which were probable candidates to be used as compatibilizers between PC and zeolites, on the performance of polycarbonate (PC) gas separation membranes was examined in this study.

These compounds had multifunctional groups and capability of interacting with polymer and zeolite. Their molecular sizes were much smaller and they were used in lower amounts compared to the ones employed in the studies mentioned in Table 2.2. In this study, PC/compatibilizer blend membranes were prepared to see the effect of compatibilizer on the membrane performance of homogenous dense polymeric membrane.

CHAPTER 3

EXPERIMENTAL

3.1. Materials for Membrane Preparation

The polymeric material used for membrane preparation was analytical grade poly(bisphenol-A-carbonate), PC, which was purchased from Aldrich. The polymer has a weight-averaged molecular weight of 64,000 and glass transition temperature, T_g, of about 150 °C. Figure 3.1 shows the repeating unit of the poly(bisphenol-A-carbonate).

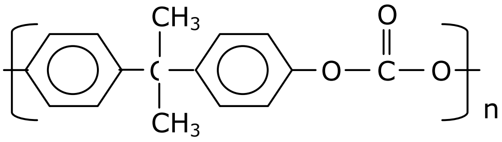


Figure 3.1 Repeating unit of poly(bisphenol-A-carbonate)

Analytical grade dichloromethane, DCM, (Aldrich) was used as solvent. It has the chemical formula of CH_2Cl_2 and the boiling point of 40 °C.

Table 3.1 lists the compatibilizers selected to prepare the membranes. All compatibilizers are analytical grade and are solid at room temperature. The compatibilizers were used in the experiments as purchased without any further treatment. Melamine, TAP and AHMP were obtained from Acros Organics and the other compatibilizers were obtained from Aldrich.

Table 3.1 Names and chemical formulas of selected compatibilizers

Name	Acronym	Chemical formula
para-nitroaniline	pNA	$C_6H_6N_2O_2$
4-amino 3-nitro phenol	ANP	$C_6H_6N_2O_3$
2-hydroxy phenol	Catechol	$C_6H_6O_2$
2-hydroxy 5-methyl aniline	HMA	C_7H_9NO
2,4,6-triamino 1,3,5-triazine	Melamine	$C_3H_{12}N_6$
2,4,6-triaminopyrimidine	TAP	$C_4H_9N_5$
2-amino 4-hydroxy 6-methylpyrimidine	AHMP	$C_5H_9N_3O$

3.2 Determination of Solubilities of Compatibilizers

The solubility of a compatibilizer in DCM was determined prior to membrane preparation. The following procedure was used: A 0.1 g of compatibilizer was added to 10 ml of DCM, the mixture was stirred by a magnetic stirrer at room temperature for at least 3-4 h. If the solution was not clear, the amount of compatibilizer was decreased and the same procedure was repeated. If a clear solution was obtained, the amount of compatibilizer was increased and the same procedure was repeated.

3.3 Membrane Preparation Methodology

Membranes were prepared by solvent evaporation method. A compatibilizer was dissolved in DCM, and then PC was added to this solution. This mixture was continuously stirred until a clear solution was obtained. The concentration of PC in DCM was kept constant at 7 w/v% for all membranes. The compatibilizer/PC ratio in the solution varied between 0.5 and 10 w/w% depending on the type of compatibilizer. Table 3.2 shows the compatibilizer/PC ratios tested for a particular type of compatibilizer.

Table 3.2 Compatibilizer/PC ratio in the membrane preparation solution

Membrane	**Compatibilizer**	**Compatibilizer/PC ratio, w/w%**
PC/pNA	pNA	0.5, 1, 2, 5, 10
PC/ANP	ANP	1, 2
PC/HMA	HMA	1,2
PC/Catechol	Catechol	1, 2, 5

The solution was drop cast on a Petri dish with a diameter of 10 cm at room temperature in air. It was allowed to dry in an oven at 0.9 atm and 55 °C ± 5 for 45 minutes in nitrogen atmosphere, then membrane was peeled from the Petri dish. The oven was again filled with nitrogen for annealing. The membrane was annealed for 24 h at 0.9 atm and 55 °C ± 5 to remove any solvent residue. After annealing the membranes were kept in a desiccator filled with dessicant silica gel. The thickness of membranes was measured by using a micrometer and that of several membranes was measured from SEM micrographs. Since both measurements showed similar results micrometer measurements were used in permeability calculations. Membrane preparation procedure was summarized in Figure 3.2.

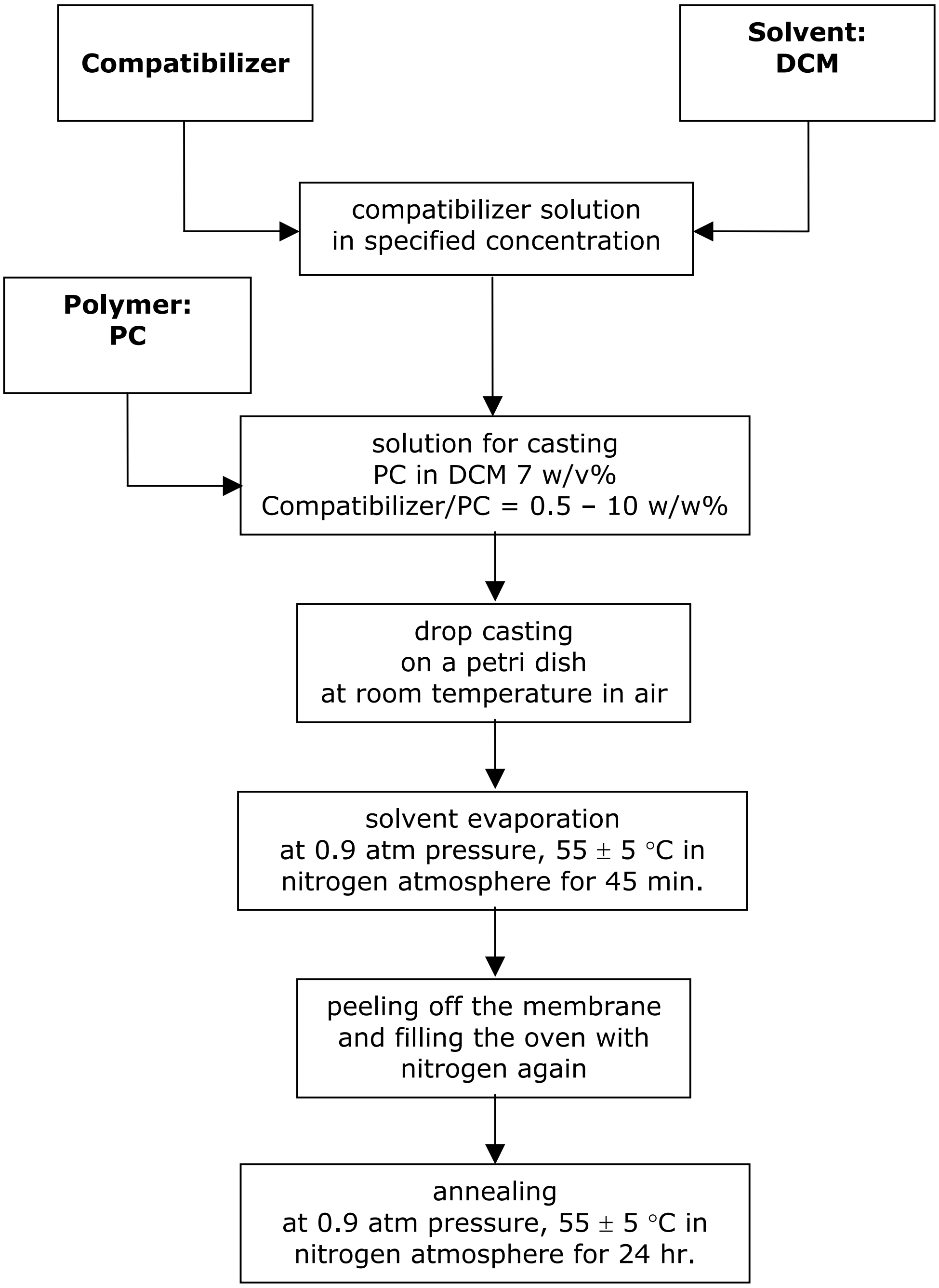


Figure 3.2 Membrane preparation procedure

3.4 Measurement of Single Gas Permeabilities

3.4.1 Experimental Set-up and Procedure

Figure 3.3 shows the schematic drawing of the experimental set-up used in the measurement of single gas permeabilities. It was previously used by our research group and the details of the set-up were explained in the related theses [24-25]. The set-up consists of a permeation cell and pressure transducer, a gas chamber and a vacuum pump. The permeation cell was located in a constant temperature silicone oil bath. The bath temperature was measured by a thermometer. The membrane that was placed in the permeation cell was supported by several sheets of filter paper and clamped between two flanges (Figure 3.4). The dead-end volume of the permeation cell was 6 cm^3 [25, 34].

Single gas permeabilities of nitrogen, hydrogen, oxygen and carbondioxide were measured at room temperature. The gases were purchased from local companies (Oksan) and their purities were higher than 99%. The measurements always began with N_2 and ended up with CO_2, because CO_2 may cause the plasticization of the membranes [35, 36].

Before each permeation measurement, both sides of the membrane were evacuated to less than 0.1 bar by a 2-stage mechanical vacuum pump (Model E2M5, Edwards High Vacuum Pump). The membrane was kept in vacuum for 1 h between two runs carried out with the same gas, and for 1.5-2 h before switching to another gas.

The experimental measurements were performed by constant volume variable pressure technique [37]. The penetrant gas was sent to the gas chamber after passing through the dehumidifier, which was filled with zeolite 4A.

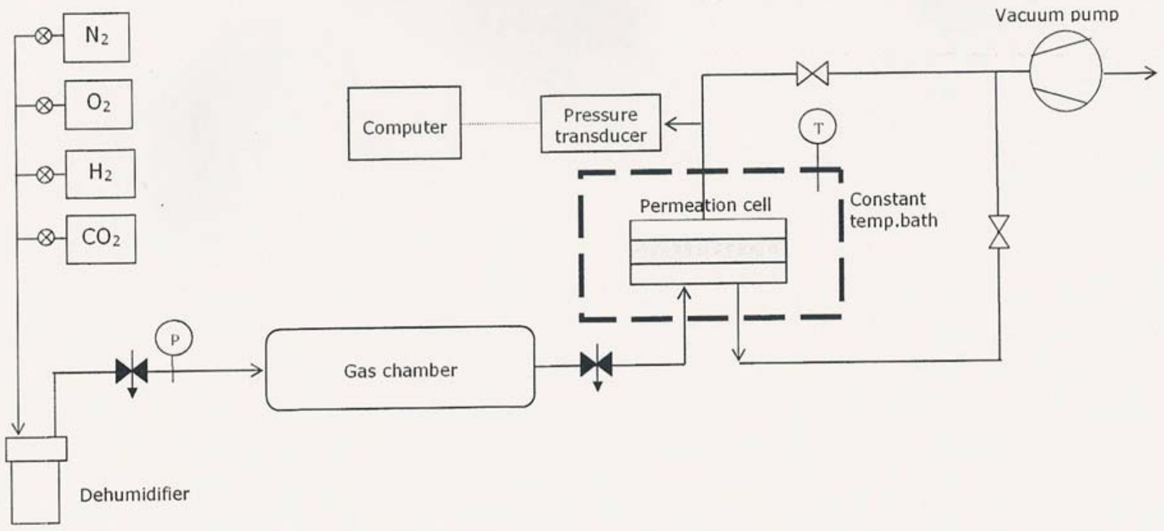


Figure 3.3 Schematic representation of gas permeation set-up

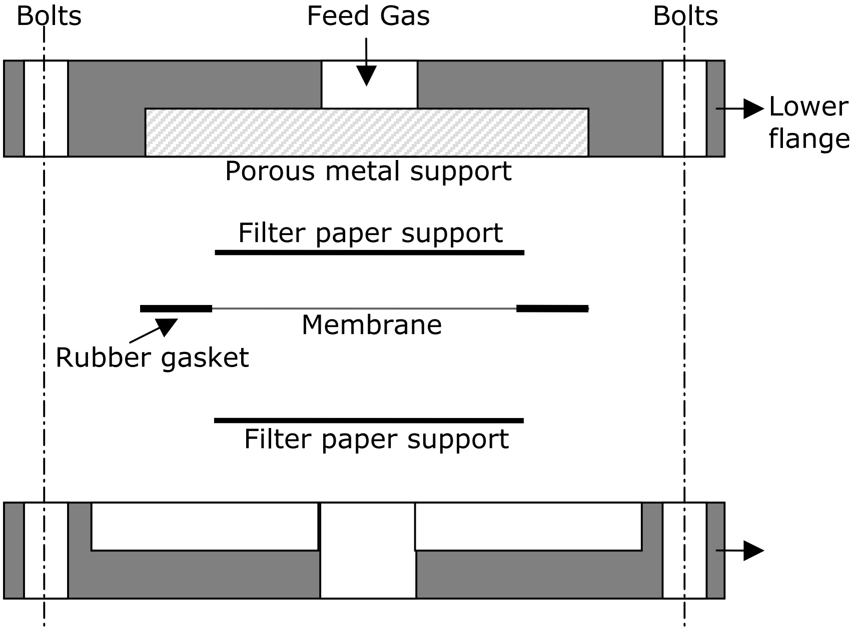


Figure 3.4 Front view of the permeation cell

The pressure was 3.7 bar in the gas chamber. Then, the gas was fed to the permeation cell at this pressure (the feed side). The initial transmembrane pressure difference was 2.7 bar. Since this is a dead-end system with no outlet for the feed except through the membrane, the pressure rise at the other side of the membrane (the permeate side) was monitored to calculate the permeability. The pressure was measured by a pressure transducer (Data Instruments, Model SA, 0 – 100 psia pressure range) with a sensitivity of 0.01 psia. The permeability of each gas through a membrane was measured twice.

3.4.2 Permeability Calculations

Permeability of a single gas through a membrane can be calculated from Equation 3.1, which is the combination of Fick's law and Henry's law.

$$P = [([\nu / A].\delta) / (p_f - p_p)] \tag{3.1}$$

where

P = permeability (barrer), 1barrer = 10^{-10} cm^3 STP.cm / cm^2.s.cmHg

ν = volumetric flow rate of the permeate gas through the membrane (cm^3/s)

A = effective membrane area (cm^2)

δ = thickness of the membrane (cm)

p_f, p_p = pressures of feed and permeate sides, respectively (cmHg)

The volumetric flow rate of the permeate gas can be found by

$$\nu = (dn/dt)\ M\ (1/\rho) \tag{3.2}$$

where dn/dt is the molar flow rate of the permeate gas, ρ is the density of the permeate gas and M is the molecular weight of the gas. Density of permeate gas is calculated by assuming ideal gas law;

$$\rho = PM/RT \tag{3.3}$$

where P is taken as the average of initial and final pressures at the permeate side.

By using the ideal gas law, the molar flow rate of the gas can be expressed as;

$$dn/dt = (dp/dt)\ (V_d/RT) \tag{3.4}$$

In this equation dp/dt is the slope of pressure versus time graph. The slope was taken on the region, where the pressure rises steadily in the permeate side. V_d is the dead volume and T is the absolute temperature. Pressure vs. time data points were fit to a straight line by linear regression method. The slope of this line (dp/dt) was used for calculation of permeabilities by Windows Excel program. The algorithm for permeability calculations was given in Appendix A.

The ideal selectivity of a membrane for a gas over another was defined as the ratio of single gas permeabilities, which can be expressed as;

$$\alpha_{ij} = P_i / P_j \tag{3.5}$$

3.5 Membrane Characterization

3.5.1 Thermal Characterization

Membranes were analyzed to determine the effect of compatibilizer type and concentration on the glass transition temperature of polycarbonate by DuPont 910S Differential Scanning Calorimeter (DSC). The samples were heated in N_2 flow from room temperature to 250 °C that is well above the glass transition temperature of the pure PC membrane (150 °C). They were then cooled to room temperature and heated again to 250 °C. The heating rate for both scans was 5°C/min and the nitrogen flow rate was 50 ml/min.

Membranes were also analyzed by a 951 Dupont Thermal Gravimetry Analyzer in order to determine the thermal stability and the amount of residual solvent. The samples were heated at a rate of 5°C/min in N_2 atmosphere. The nitrogen flow rate was 70 ml/min.

3.5.2 Fourier Transform Infrared Spectrometry (FTIR) Characterization

FTIR spectra of membranes were obtained by using Brucker Equinox 55 model FTIR spectrometer. Compatibilizers in powder form were mixed with potassium bromide salt in the ratio of 1:100 approximately, and then pressed into disk shape before taking their spectra. Membranes were analyzed in the film form. Spectrometer was calibrated with polyethylene film and measurements were performed against to air in the range of 4000–400 cm^{-1} wavenumber (mid-infrared).

3.5.3 Scanning Electron Microscopy (SEM) Characterization

Membrane morphology was determined by Scanning Electron Microscopy (SEM) on a JEOL JSM-6400. Membranes were fractured in liquid nitrogen to obtain a clean break and a smooth section for micrography. The samples were then stuck vertically on to a circular aluminium sample holder to observe the cross sectional morphology. The samples were coated with gold in order to provide an electrically conductive layer, to minimize radiation damage, and to increase electron emission [38]. After coating, the membranes were analyzed at a magnification of 1500x.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Selection of Materials

Polymer / zeolite MMMs have potential for efficient separation of gas mixtures. However, the incompatibility between zeolite crystals and polymer chains leads to formation of non-selective voids in the membranes, so that the membrane performance decreases. A low molecular weight substance with multifunctional groups, which may connect the zeolite and the polymer can be used as compatibilizer to improve the separation performance of MMMs.

In this study, the effect of a number of compatibilizers on polycarbonate matrix was investigated without adding zeolites into the membrane. Polycarbonate (PC) is an attractive commercially available polymer for preparing gas separation membranes because it allows fast gas permeation rates with reasonable selectivities [39-41]. For example, it shows high O_2 permeability with O_2/N_2 selectivity near the upper bound line on the middle region of Robeson plot, which is usually applied to evaluate the performance of polymeric membranes [3, 41]. Gülşen and Hacarlıoğlu [24, 25] prepared polycarbonate MMMs with conductive polymeric fillers and obtained high selectivities for O_2/N_2 and H_2/N_2. They showed that PC could be an appropriate polymer for preparing MMMs.

Polycarbonate has also high glass transition temperature and provides the necessary backbone rigidity for good thermal resistance and mechanical behaviour [42, 43]. Because of these reasons, PC was selected as matrix polymer in this study.

Hacarlıoğlu [24] also studied the effect of type of solvent and concentration on the gas separation performance of pure PC membranes. She showed that membranes prepared from solutions with a composition of 7 w% PC in DCM exhibited good performances in H_2/N_2 and O_2/N_2 separation. Therefore, DCM was used as solvent and the concentration of PC in DCM was kept constant at 7 w% throughout the study.

The candidate chemicals listed in Table 4.1 were chosen for use as compatibilizer based on literature [14] and following criteria:

- have multifunctional groups capable of interacting with PC and zeolite,
- be soluble in DCM, which is used to prepare polymer solution,
- have high melting point to produce stable membrane structure in addition to prevent evaporation of the compound during membrane annealing,
- have low molecular weight to interact simultaneously with polymer and zeolite.

Chosen candidate chemicals have amine, nitro and hydroxyl functional groups, as shown in Table 4.1. Hydroxyl groups can bind the compatibilizer to the zeolite surface [11, 13] and the compatibilizer may attach to polymer chain from amine and nitro groups by hydrogen bonding [14]. Yong et al. claimed that the carbonyl group of polyimide and the amine group of 2,4,6-triaminopyrimidine forms hydrogen bond. Paul et al. [15] modified polysulfone membranes with fluorene based additives, such as fluorene bisphenol which has two phenol groups superimposed on fluorene. The polymer and the additive linked to each other by hydrogen bonding through the hydroxyl groups of additives.

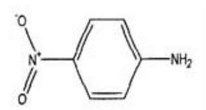
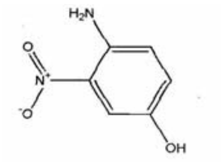
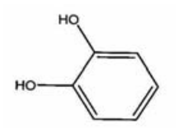
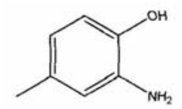
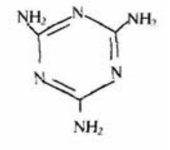
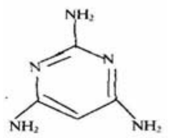
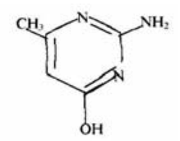
The compatibilizers given in Table 4.1 are low molecular weight compounds, which may fill the voids formed in the membrane matrix. All compounds have high melting point, therefore stable membrane structures can be obtained after evaporation of the solvent.

Solubilities of these substances in DCM were determined experimentally at room temperature. Catechol was highly soluble in DCM. Similarly, pNA and HMA showed sufficient solubility. The solubilities of melamine, TAP, ANP and AHMP were, however, not sufficiently high in DCM. The solubility of them was less than 0.25 w/v% at room temperature. Based on the solubility results as well as the physical properties of the compatibilizers, pNA, Catechol and HMA were selected to prepare PC/compatibilizer blend membranes.

The studies started with pNA. It has two functional groups in para position, therefore possible intramolecular interactions between them can be eliminated and the compatibilizer is expected to interact with the polymer chain. ANP was also studied as a compatibilizer although it has low solubility. It has a similar chemical structure with pNA but amine and nitro groups are in ortho position to each other and it has an additional functional group of hydroxyl. Therefore, the effect of hydroxyl group on the PC matrix can be studied.

Compatibilizer concentration was held at low values (0.5-10 w% of PC) in membrane matrix to eliminate any problems caused by their low solubility in

Table 4.1 Experimental solubilities of selected compatibilizers with their physical properties

Acronym & Chemical formula	**Structure**	**Molecular Weight [44]**	**Melting Point (°C) [44]**	**Boiling Point (°C) [44]**	**Solubility in DCM at room temperature (this study)**
pNA $C_6H_6N_2O_2$		138.13	148.5	331	2 w/v %
ANP $C_6H_6N_2O_3$		154.11	154	NR*	0.25 w/v %
Catechol $C_6H_6O_2$		110.11	105	245	> 3w/v %
HMA C_7H_9NO		123.16	137	NR	1 w/v %
Melamine $C_3H_{12}N_6$		126.12	> 250 (decomp. at 354 °C)	sublimes	< 0.25 w/v %
TAP $C_4H_9N_5$		124	250	NR	< 0.25 w/v %
AHMP $C_5H_9N_3O$		125.13	> 250	NR	< 0.25 w/v %

* NR: Not reported

DCM and since they were planned to be used only as additives to increase polymer zeolite compatibility not as major components of membranes.

4.2 Permeability Results of Pure PC Membranes

4.2.1 Evaluation of Pressure-Time Raw Data

The permeability of single gases through pure PC membranes was measured in a dead-end system at room temperature. The feed side pressure was 3.7 bar and the permeate side pressure was initially at atmospheric pressure (~0.9 bar). The pressure rise at the permeate side with time was shown in Figure 4.1.

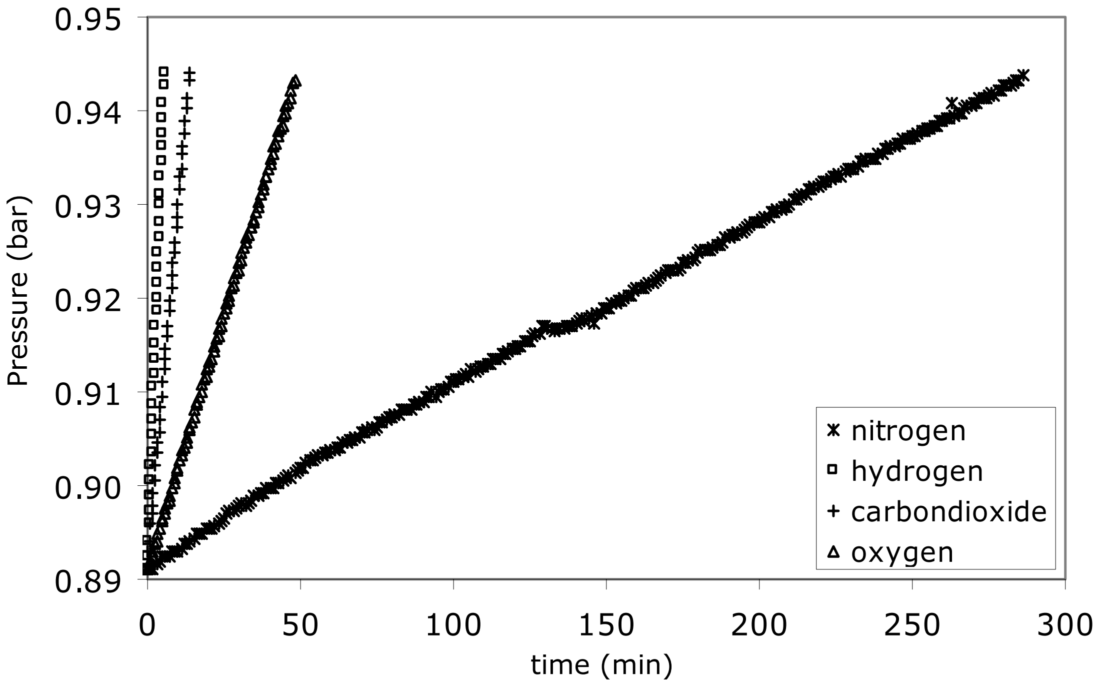


Figure 4.1 Permeate side pressure-time data for pure PC membrane

Permeability measurements always began with nitrogen and ended with carbondioxide to avoid from the plasticization effect of carbondioxide on PC membrane matrix [35, 36]. The permeate side pressure increased steadily for all gases. The pressure reached 0.95 bar in approximately 8 min during the hydrogen permeation, and in 15 min in the carbondioxide permeation, however, this period was 48 min and 280 min for oxygen and nitrogen, respectively. The order of permeabilites was hydrogen > carbondioxide > oxygen > nitrogen.

4.2.2 Permeability Calculations

Permeabilities were calculated by fitting all pressure-time data on a straight line by linear regression method. The slope of this line was used to find membrane's permeability as described in Section 3.4.2 and Appendix A.1.

The same data were also used to calculate the permeabilities for small constant time intervals (or pressure intervals) to determine the change of permeability during the experiment. Figure 4.2 shows H_2 permeability calculated at every 30 s of permeation and at times that corresponds to every 3 mmHg rise of permeate side pressure. For each interval, the permeability was calculated by linear regression method and the average permeability of the gas through the membrane was found by taking the arithmetic average of them. A sample calculation was given in Appendix A.2.

Both methods showed a similar trend and the permeabilities fluctuated around the average hydrogen permeability of 10.45 barrer. The maximum deviation from the average was observed at the beginning of the experiment (up to 2 min).

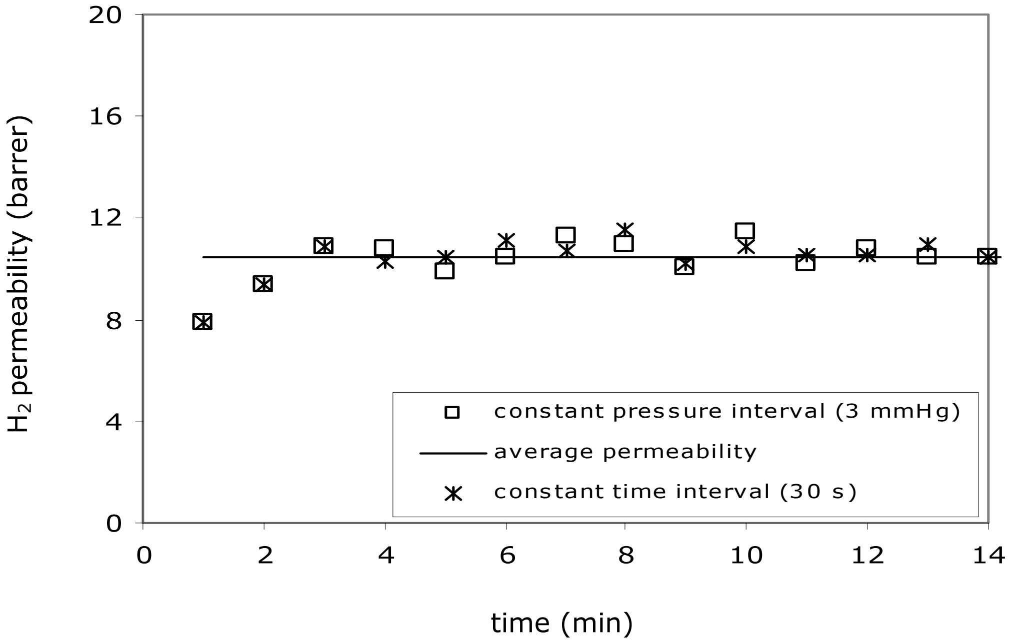


Figure 4.2 The change in H_2 permeability for constant time and pressure intervals

Table 4.2 Permeability results for N_2 and H_2 calculated by different methods for pure PC membrane

Methods	Permeability (barrer)	
	N_2	H_2
linear regression fitting	0.238	10.67
constant time interval	0.224	10.40
constant pressure interval	0.237	10.45
Average	0.233	10.51
relative standard deviation, %	3.34	1.37

This was probably due to time-lag caused by adsorption of gas molecules to the membrane, which led to increase in permeability during the first two minutes of experiment. The insufficient sensitivity of pressure transducer at low pressure can be another reason of this increase.

Average permeability calculated with three methods were compared in Table 4.2 for H_2 and N_2. Both methods yielded similar results with a relative standard deviation of 1.37 for H_2 and 3.34 for N_2. Since the relative standard deviations were small the first method (fitting all data on a straight line) was used in permeability calculations for other membranes.

4.2.3 Reproducibility In Permeability Measurements and Membrane Preparation

In order to obtain reliable results, reproducible membrane preparation and repeatable permeability measurements have great importance. Therefore, a series of reproducibility experiments was carried out. Four membranes which were prepared at different times but under similar conditions were tested in a single gas permeation set-up. For each membrane, permeability of each gas was measured at least two times. Thus, the repeatability of permeability measurements and the reproducibility of membrane preparation were examined.

The results for pure PC membranes were shown in Table 4.3. Permeability measurements were always done in the sequence of N_2, H_2, O_2 and CO_2 and at room temperature. The thickness of the membranes changes between 40-55 μm. For each membrane, nitrogen permeability was measured three times while oxygen, hydrogen and carbondioxide measurements were repeated two times. Membranes were degasified by evacuating the membrane cell between measurements. The ideal selectivities were calculated by dividing the average permeability to nitrogen permeability.

Relative standard deviation between the runs for N_2 was in between 1.2-2.4%, for H_2 in between 0.41-0.89%. Hydrogen permeability measurements

Table 4.3 Permeability and selectivity results for pure PC membranes measured at room temperature

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
M1 (40 µm)	1	0.266	11.51	1.39	5.54			
	2	0.272	11.36	1.37	5.57			
	3	0.267	-	-	-			
	avg.	0.268	11.44	1.38	5.56	42.7	5.2	20.8
	std. deviation	1.19	0.76	1.02	0.38			
M2 (50 µm)	1	0.261	10.95	1.67	5.14			
	2	0.254	11.09	1.60	5.25			
	3	0.255	-	-	-			
	avg.	0.257	11.02	1.64	5.18	42.9	6.9	20.2
	std. deviation	1.47	0.89	3.02	1.50			
M3 (50 µm)	1	0.284	11.51	1.31	5.21			
	2	0.273	11.40	1.29	5.24			
	3	0.285	-	-	-			
	avg.	0.281	11.46	1.3	5.23	40.8	4.6	18.6
	std. deviation	2.37	0.62	1.09	0.41			
M4 (55 µm)	1	0.255	12.13	1.47	5.79			
	2	0.259	12.20	1.51	5.88			
	3	0.252	-	-	-			
	avg.	0.255	12.17	1.49	5.84	47.7	5.8	22.9
	std. deviation	1.38	0.41	1.89	1.09			
AVG.		0.265	11.52	1.45	5.45	43.5	5.6	20.6
Relative standard deviation,%		4.9	4.1	3.7	5.7	6.8	17	8.6

were more precise than nitrogen because hydrogen permeated more quickly than nitrogen and pressure increase in the permeate side can be sensed more accurately by the pressure transducer. The small differences between the measurements indicated that measurements had good repeatability.

Table 4.3 also shows the average of four membranes and standard deviation in their permeability. Relative standard deviation between the membranes was found as 4.9% for N_2, 4.1% for H_2, 3.7% for O_2 and 5.7% for CO_2 permeability. When this deviation was calculated on the basis of selectivities it increased to 6.8% for H_2/N_2, 17% for O_2/N_2 and 8.6% for CO_2/N_2. These results showed the reproducibility in membrane preparation was very high. The slight differences between the membranes were probably coming from the factors affecting membrane preparation, such as homogenous polymer solution preparation, solvent evaporation and annealing conditions.

Table 4.4 Permeabilities for dense homogenous PC membranes in literature

Reference	T (°C)	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
Norton [45]	25	0.300	12.00	1.40	8.00	40.00	4.70	26.70
Chan et al [46]	35	0.255			6.65			26.10
Muruganandam et al [47]	35	0.289		1.48	6.00		5.13	20.80
Barbari et al [48]	35	0.280		1.48	6.00		5.30	21.43
Hellums et al [49]	35	0.330		1.60	6.80		4.85	20.60
Barbari et al [41]	35	0.270		1.50	6.48		5.56	24.00
Hellums et al [50]	35	0.330		1.60	6.80		4.85	20.60
Haraya et al [39]	25	0.210		1.17			5.57	
Aguilar-Vega et al [51]	35	0.290		1.48	7.54		5.10	26.00
Ruaan et al [52]	NR*	0.250		1.00			4.00	
Chen et al [53]	NR	0.320		1.80			5.63	
Chen et al [40]	NR	0.240		1.50			6.25	
This study	25	0.265	11.52	1.45	5.45	43.5	5.60	20.60

* NR: Not reported

The permeability and selectivity results obtained for pure PC membrane were compared with those given in the literature in Table 4.4.

All studies showed that the fastest gas permeating through the pure PC membranes is hydrogen and the slowest gas is nitrogen. Although the trends were similar the permeability and selectivity data obtained from literature showed significant differences. The permeability values are in the range of 0.210-0.330 barrer for N_2, 1.00-1.80 barrer for O_2 and 6.00-8.00 barrer for CO_2. The O_2/N_2 selectivities change between 4.00-6.25 and the CO_2/N_2 selectivities change between 20.60-26.70. These differences may be attributed to the differences in gas permeation measurement and membrane preparation parameters which are the type and concentration of casting solvent, solvent evaporation temperature and period, annealing temperature and period. Although the performance of the membranes strongly depends on membrane preparation parameters as shown by Hacarlıoğlu [24], the values for these parameters have not been reported in many studies. Table 4.4 also shows the average permeabilities and selectivities for PC membranes prepared in this study. The permeabilities and selectivities compare well with those reported in the literature.

Based on these results, it can be concluded that the procedure developed for membrane preparation is successful and yields reproducible membranes. The results also showed that the membrane testing system and methodology were reliable.

4.3 Effect of Compatibilizers on PC Membrane Performance

4.3.1 PC/pNA Membranes

Membranes with compatibilizers were prepared from solutions containing 7 w% PC in DCM. The compatibilizer/PC ratio was varied in the range of 0.5-10 w/w%. Permeability measurements through these membranes were carried out with N_2, H_2, O_2 and CO_2 at room temperature.

The permeabilities of gases were plotted with respect to increasing pNA concentration of PC/pNA membranes (Figures 4.3 to 4.6). The permeabilities of all gases through pNA added membranes were lower than those through pure membrane, although membranes contained very small amount of pNA.

The permeabilities of all gases decreased with increasing pNA concentration. The permeability decrease was sharp up to 2 w% pNA concentration, and above this concentration it was slower. The permeability of H_2, however, decreased slowly with increasing pNA content of the membrane. The largest decrease was observed in N_2 permeability. Its permeability decreased from 0.26 barrer to 0.10 barrer with the addition of 2 w% pNA. In contrast the smallest decrease was observed in H_2 permeability. The H_2 permeability for pure PC membrane was 11.5 barrer while that of PC membrane with 2 w% pNA was 9.6 barrer. The decreasing order of permeabilities of gases was parallel with increasing order of kinetic diameters (Table 4.5) as in the case of pure PC membrane.

Table 4.5 Kinetic diameters of studied gases [14]

GAS	N_2	O_2	CO_2	H_2
Kinetic diameter (nm)	0.364	0.346	0.33	0.289

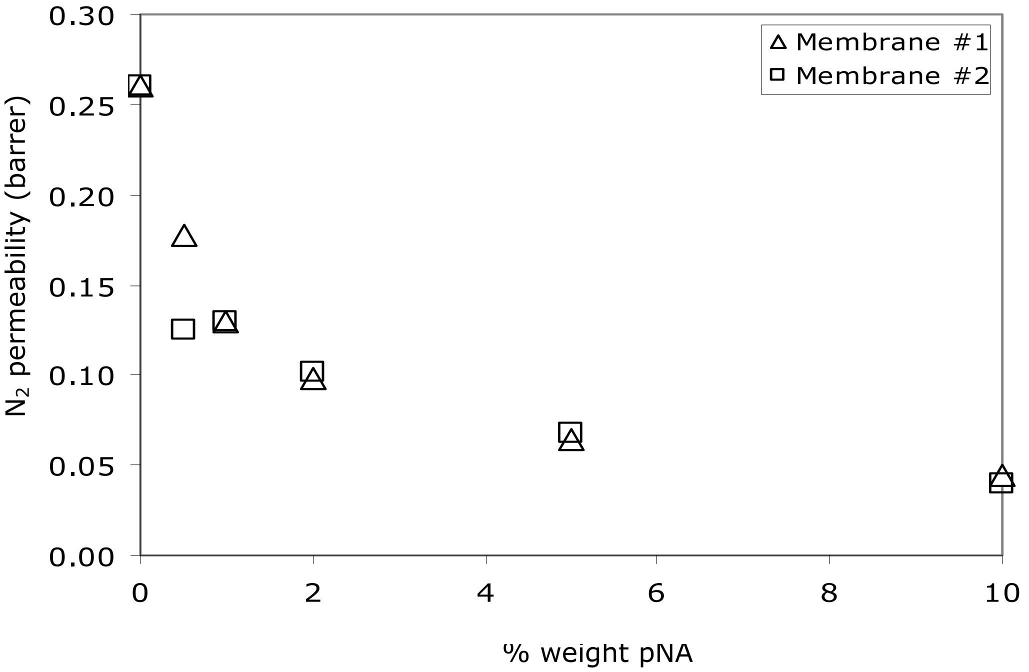


Figure 4.3 The change in N_2 permeability with pNA concentration, measured at room temperature, feed side pressure was 3.7 bar.

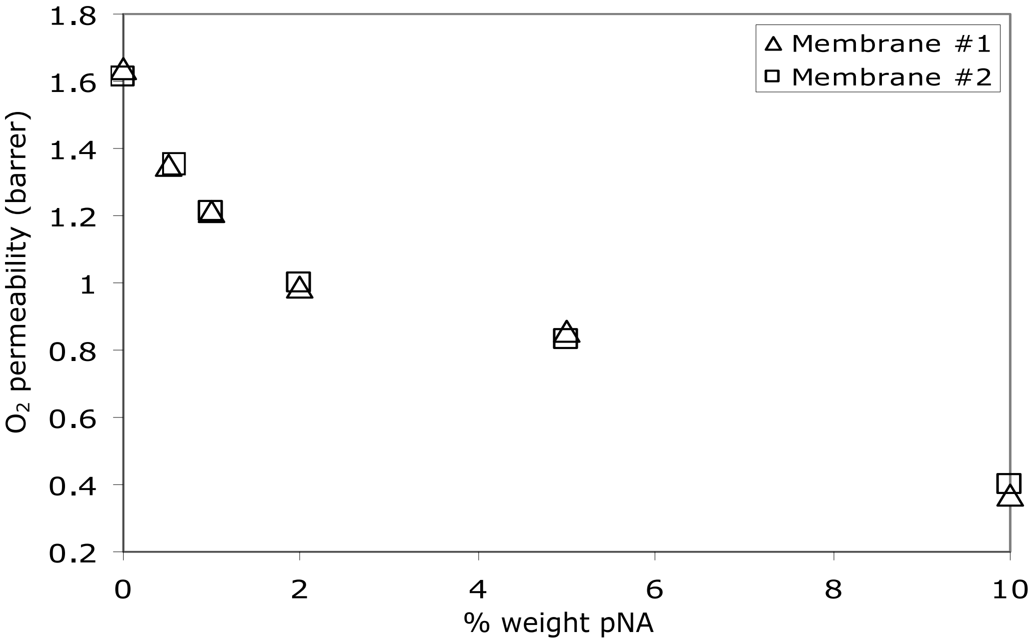


Figure 4.4 The change in O_2 permeability with pNA concentration, measured at room temperature, feed side pressure was 3.7 bar.

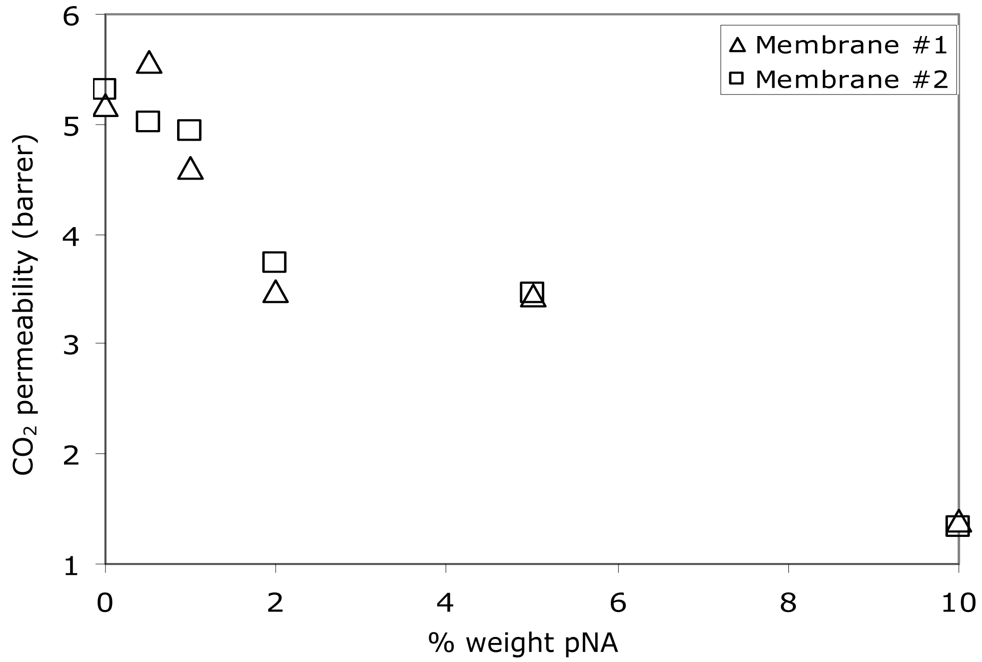


Figure 4.5 The change in CO_2 permeability with pNA concentration, measured at room temperature, feed side pressure was 3.7 bar.

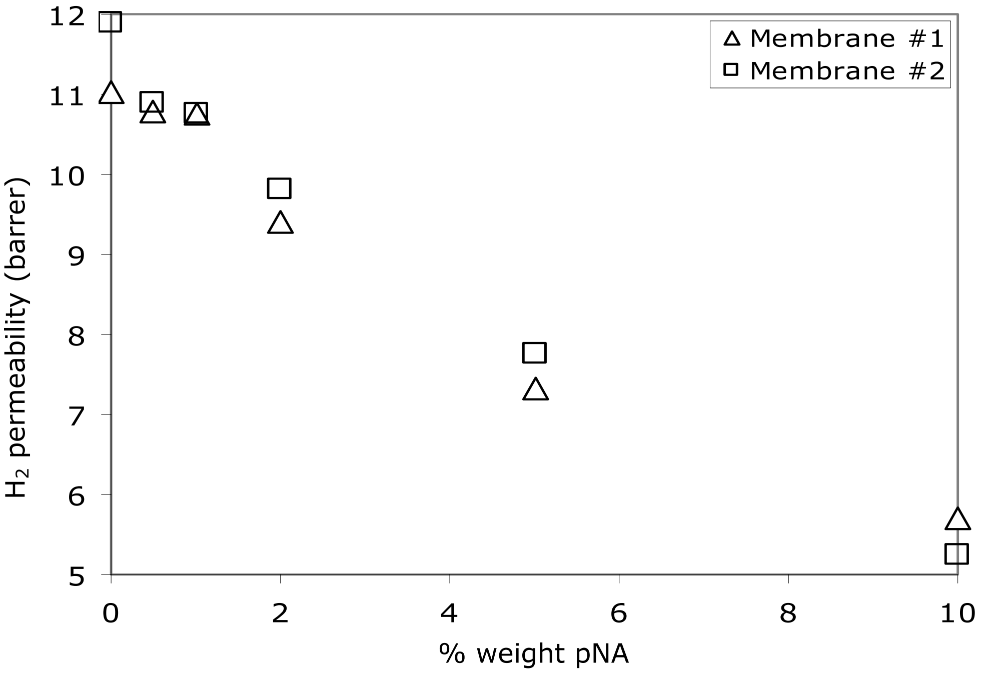


Figure 4.6 The change in H_2 permeability with pNA concentration, measured at room temperature, feed side pressure was 3.7 bar.

In the Figures 4.3 to 4.6 the results for two membranes were given for each pNA concentration. The membranes were prepared at the same conditions but at different times. The results were also tabulated in Appendix B. There was no significant difference between the permeabilities through the membranes, except the 0.5 w% pNA/PC membrane. Apparently, the membrane preparation method is reproducible. The concentration of pNA in 0.5 w% pNA/PC membrane was very low, therefore some unpredicted errors might have occurred during membrane preparation.

Membrane selectivities were calculated and plotted against to increasing concentration of pNA. They are presented in Figure 4.7 to 4.9. Although the compatibilizer concentration in the membrane was very low, the selectivities for all gas pairs increased considerably with increasing concentration of pNA. The highest increase was observed for H_2/N_2 selectivity which increased from 43.5 to 96.5 with the addition of 2 w% pNA and to 130 with the addition of 10 w% pNA. The increase in CO_2/N_2 selectivity follows H_2/N_2 selectivity and the lowest increase was observed for O_2/N_2 selectivity.

The increase in selectivities were very fast up to 2 w% pNA for all gas pairs, above that concentration the rate of increase in selectivities was slow. Except H_2/N_2, selectivities of CO_2 over N_2, and O_2 over N_2 exhibited a maxima at around 5 w% pNA concentration. In 10 w% pNA/PC membrane, pNA dispersed unevenly and formed visible small agglomerates throughout the membrane matrix probably due to the limited solubility of pNA in DCM and its limited miscibility with PC. As the solvent evaporated, precipitation limit may be exceeded before solidification of homogenous PC/pNA blend membrane. Effect of molecular structure formed in this extreme conditions is different on selectivity of H_2/N_2 probably due to very small size of H_2.

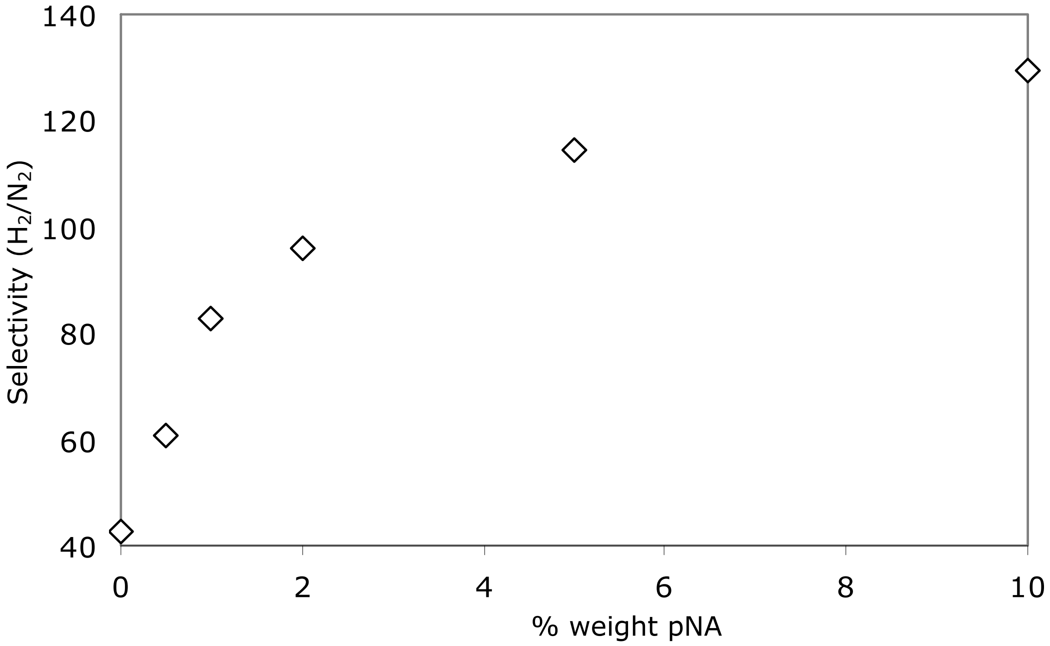


Figure 4.7 Effect of pNA concentration on H_2/N_2 selectivity

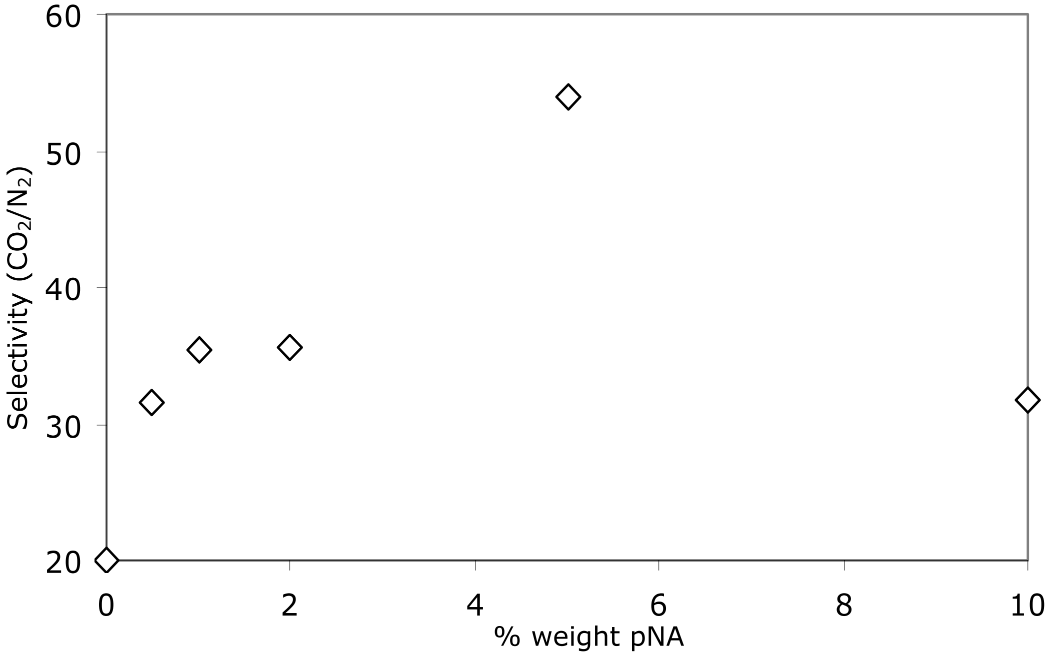


Figure 4.8 Effect of pNA concentration on CO_2/N_2 selectivity

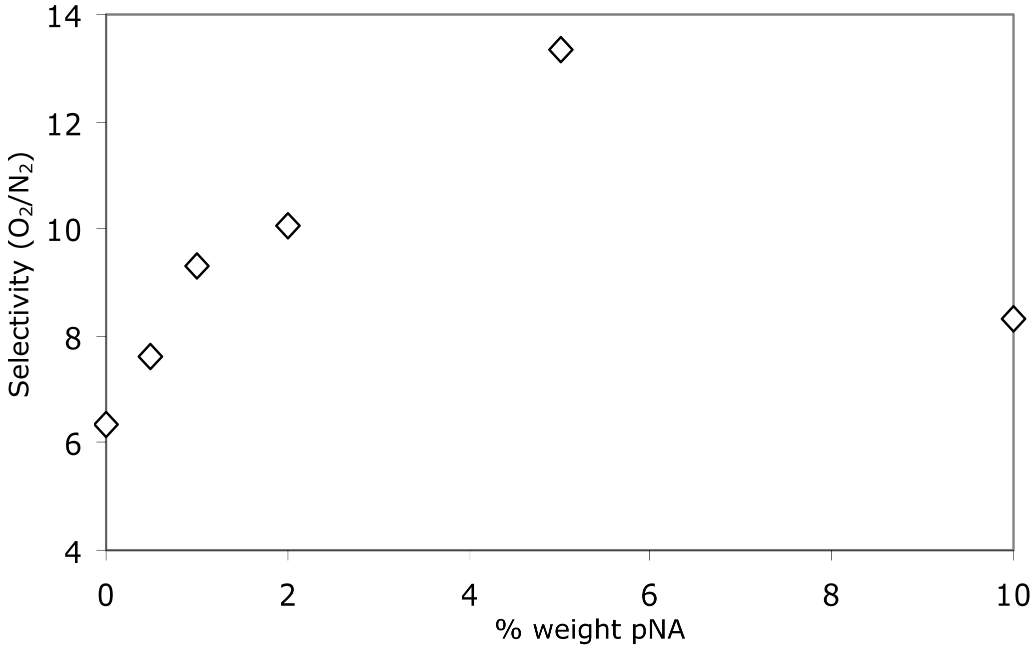


Figure 4.9 Effect of pNA concentration on O_2/N_2 selectivity

The decreasing behaviour of permeabilities with the addition of compatibilizers is similar to the results of Yong et al. [14]. They prepared polyimide (PI) membranes with 2,4,6-triaminopyrimidine (TAP), which was used as compatibilizer. The TAP/PI ratio in the membrane was 21 w/w%. This concentration is very high compared to compatibilizer concentration examined in this study. They observed that PI/TAP membranes showed lower permeabilities but higher selectivities than pure PI membranes, e.g. nitrogen permeability decreased from 0.218 to 0.0022 barrer and O_2/N_2 selectivity increased from 6.88 to 15.4. This decrease in permeabilities was explained by decrease in free volume as a result of hydrogen bond formation between the amine groups of TAP and carbonyl groups of PI.

It is also known that antiplasticizers decrease the permeabilities of gases through glassy polymers [27-29]. Naphthalene, sebacate and phthalate based compounds are commonly used as antiplasticizers. Addition of 30 w% N-phenylnaphthylamine as antiplasticizer to polysulfone polymer caused a decrease in permeability of hydrogen from 13.8 to 1.7 barrer and in permeability of nitrogen from 0.25 to 0.007 barrer but resulted in an increase in the H_2/N_2 selectivity from 55.2 to 242.9 [16]. Molecular sizes of these substances are bigger than the compatibilizers used in this study and their concentration in the membrane was higher. Antiplasticizer/polymer ratio changed between 10-40 w/w% in the membranes [27-29]. Antiplasticization is defined as decreasing flexibility (or increasing stiffening) of polymers with the addition of a low molecular weight compound due to reduced rates of segmental motions in the polymer chain and hence reduced the free volume in the polymer [31-33]. This effect has been shown to appear by a decrease in permeabilities of gases and increase in selectivities. The pNA caused the gas permeabilities to decrease, as antiplasticizers do, therefore, it can be concluded that pNA acted as an antiplasticizer in the PC membrane matrix.

Permeability and selectivity results clearly showed that successful blend membranes were obtained with the addition of pNA into PC membrane matrix. Although the compatibilizer concentration in the membrane was very low PC/pNA blend membranes showed enhanced selectivities for commercially important gas pairs, O_2/N_2 and H_2/N_2 compared to pure PC membrane. In Figure 4.10 the H_2 permeability and H_2/N_2 selectivity results of the PC/pNA membranes prepared at different pNA concentrations was presented with the upper bound relationship for H_2/N_2 proposed by Robeson [5]. The region of improved trade-off was defined as the above or to the right of upper bound line. Pure PC membrane located below this line. Increased addition of pNA pushed the performance of PC toward the upper bound line and this improvement was achieved with the addition of very small concentration of pNA (1-2 w%). In Figure 4.11 the O_2/N_2 selectivity versus O_2 permeability was drawn for PC/pNA membrane on a upper bound curve [3]. PC/pNA membranes showed the permeation characteristics

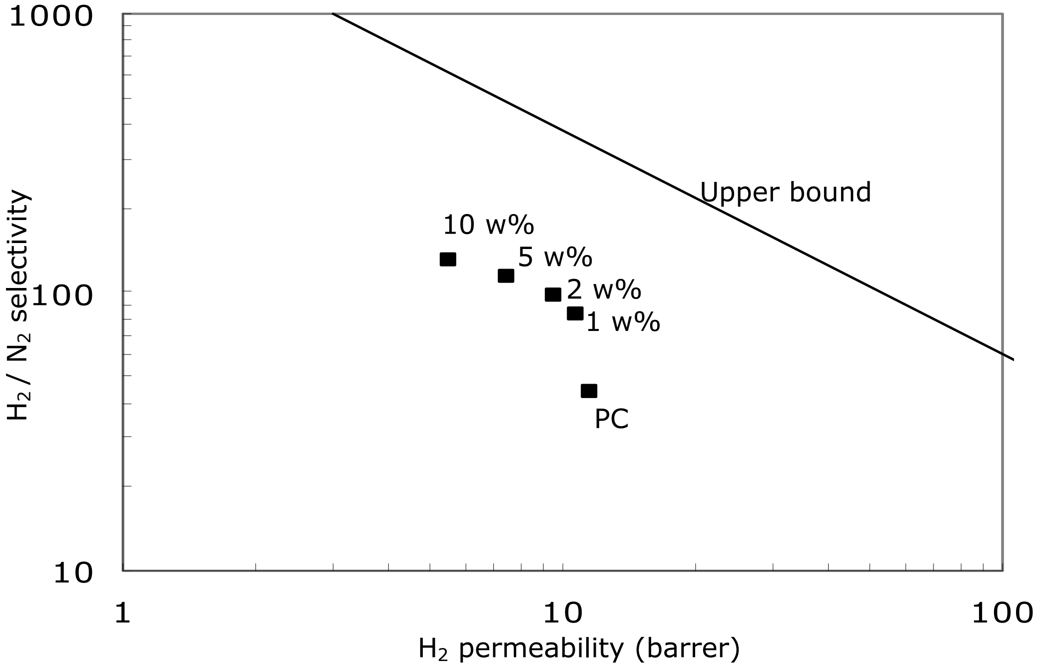


Figure 4.10 H_2/N_2 selectivity and H_2 permeability of PC/pNA blend membranes on upper bound trade off curve.

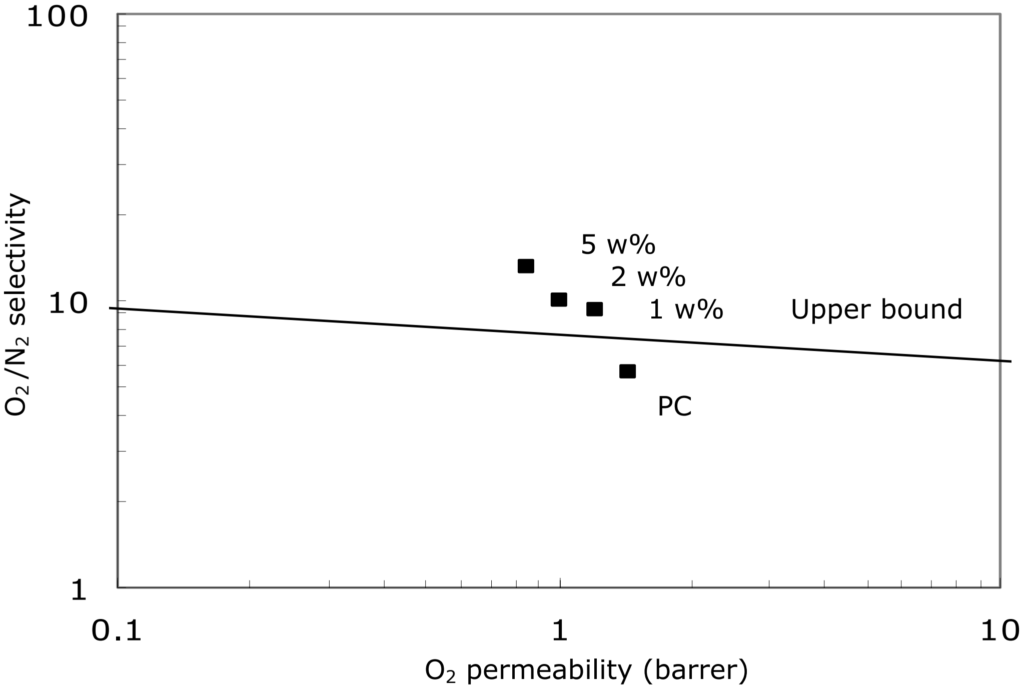


Figure 4.11 O_2/N_2 selectivity and O_2 permeability of PC/pNA blend membranes on upper bound trade off curve.

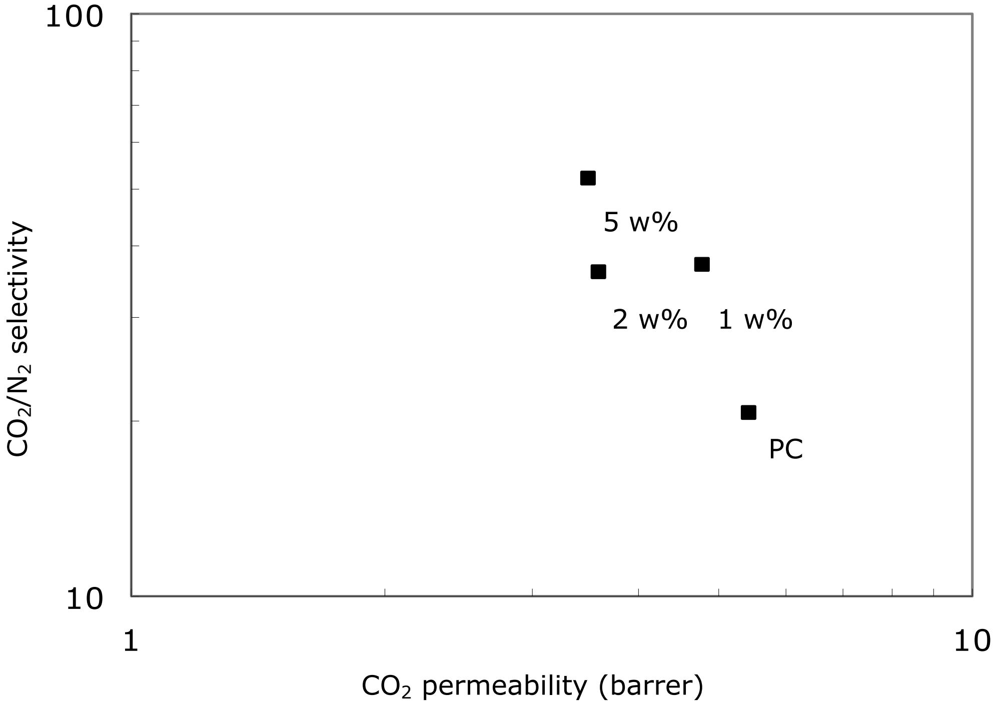


Figure 4.12 CO_2/N_2 selectivity and CO_2 permeability of PC/pNA blend membranes

located over the upper bound line for O_2 and N_2 pair.In Figure 4.12 CO_2/N_2 selectivity versus CO_2 permeability was illustrated. Although upper bound line was not drawn, a similar improvement trend was observed for this gas pair.

4.3.2 PC Based Membranes with Other Compatibilizers

Membranes by blending PC with other compatibilizers, ANP, Catechol and HMA, were prepared by using same procedure and their single gas permeabilities were measured. To observe the effect of chemical structure of compatibilizer the membranes were prepared at a constant compatibilizer/PC ratio of 1w/w%. According to the results obtained from pNA/PC membranes, 1 w% compatibilizer concentration was sufficient to change the performance of PC membrane. In addition, solubilities of ANP and HMA were low in DCM to prepare membranes at higher compatibilizer concentrations.

Permeability and selectivity results of PC membranes casted with different compatibilizers were given in Table 4.6. Their reproducibility results were given in Appendix B. Although chemical structures of compatibilizers were different, they all decrease the N_2 permeability and increase the selectivities of H_2/N_2, O_2/N_2, CO_2/N_2.The most significant decrease of N_2 permeability was seen in PC/pNA blend membrane. The N_2 permeabilities including PC/pNA and pure PC membrane decreased in the order of pure PC < Catechol < HMA ~ ANP < pNA. There was no significant change in permeabilities of H_2, CO_2 and O_2 for the membranes prepared with ANP, HMA and Catechol. However, PC/pNA blend membrane indicated a slight decrease in permeabilities for these gases.

Table 4.6 Permeability and selectivity results for PC membranes with different compatibilizers (Compatibilizer / PC = 1w/w%)

Membrane	Permeability (barrer)				Selectivity (X/N_2)		
	N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
Pure PC	0.27	11.50	1.45	5.45	42.6	5.4	20.2
PC / pNA	0.13	10.76	1.21	4.78	82.8	9.3	36.8
PC / HMA	0.16	11.98	1.41	6.1	74.9	8.8	38.1
PC / ANP	0.16	11.40	1.45	5.77	71.3	9.1	36.1
PC / Catechol	0.18	12.29	1.63	6.62	68.3	9.1	36.8

Since the selectivities were given with respect to N_2 and its permeability decreased for all PC/compatibilizer systems, the selectivities increased compared to pure PC membrane. The greatest increase in selectivity was observed for H_2/N_2 pair, then CO_2/N_2 pair came and O_2/N_2 followed it. The highest increase in selectivity of H_2/N_2 pair may be due to the smallest size of hydrogen. The increasing order of selectivities for H_2/N_2 pair is pure PC < Catechol < HMA ~ ANP < pNA.

Although the compatibilizers, pNA, ANP, HMA and Catechol had different chemical structure, they all had similar effect on the performance of PC membrane. They decreased the N_2 permeability and increased the selectivities, which indicated an interaction between PC and functional groups of compatibilizers. They were added at very low concentration and this concentration was sufficient to change the molecular structure of PC membrane. They all stiffen the membrane structure as antiplasticizers [15, 16].

4.4 Membrane Characterization

4.4.1 SEM Experiments

The SEM images of the cross sections of pure PC membrane and PC/pNA membranes with respect to increasing pNA concentration are shown in Figure 4.13. All micrographs magnified 1500 times.

Morphologies off all of the membranes were dense and no pores were observed at this magnification. The figures also showed that PC/pNA blend membranes are homogenous except the membrane with PC/pNA ratio of 10 w%. At this concentration phase separation of pNA took place, which was also observed visually. As the solvent evaporated, pNA became insoluble in the matrix and remained as discrete entities. Therefore, this percentage was taken

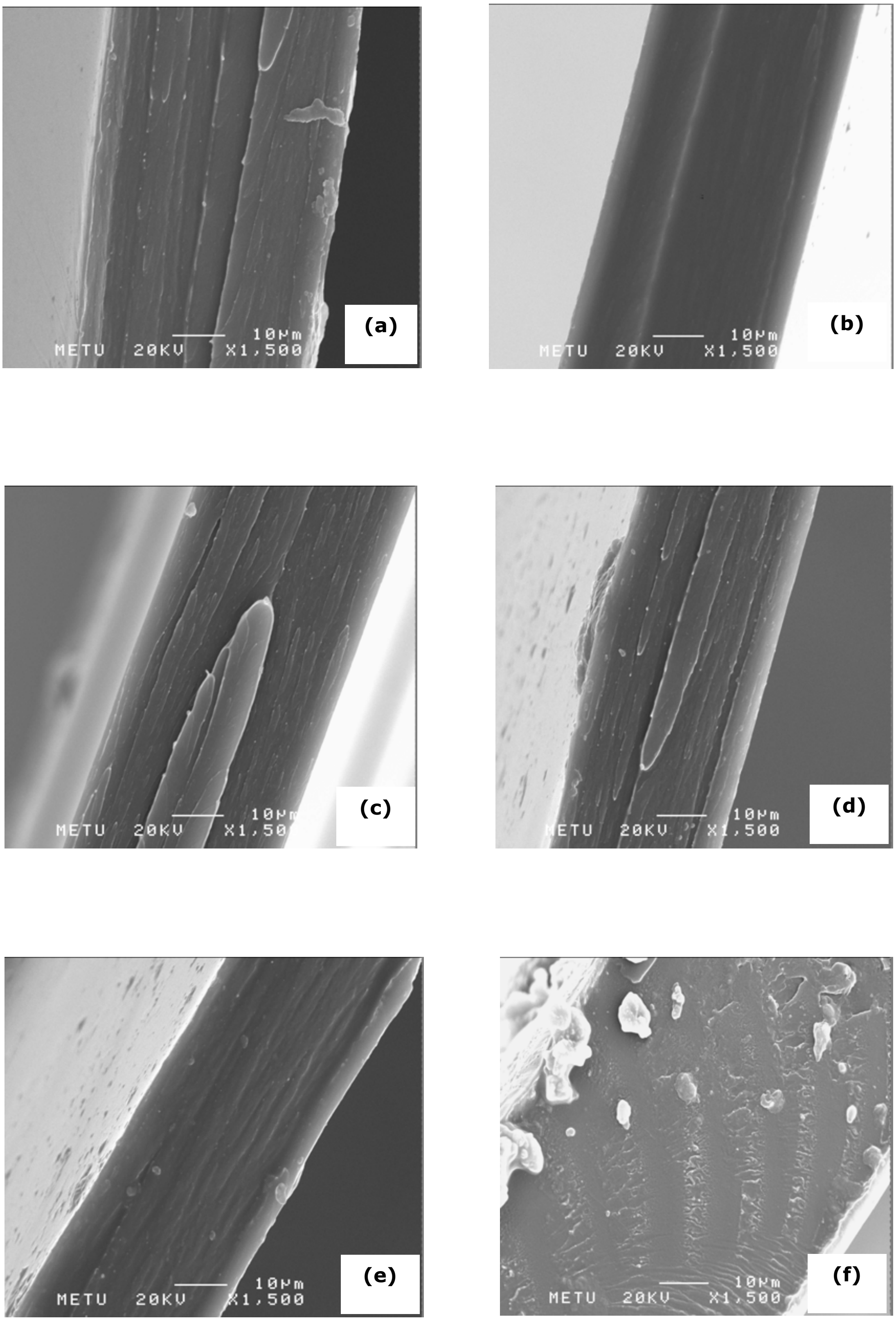


Figure 4.13 SEM micrograph for (a) pure PC, (b) PC/pNA (0.5%), (c) PC/pNA (1%), (d) PC/pNA (2%), (e) PC/pNA (5%), (f) PC/pNA (10%).

as the upper limit in PC/pNA membrane preparation. In some micrographs, the channel-like structures were observed, this may due to the surface damage of the samples when they were breaking in the liquid nitrogen.

Cross sectional morphologies of the membranes prepared with ANP, Catechol and pNA at a constant compatibilizer/PC ratio of 1 w/w% were shown in Figure 4.14. They also formed homogenous compatible blends with PC polymer matrix.

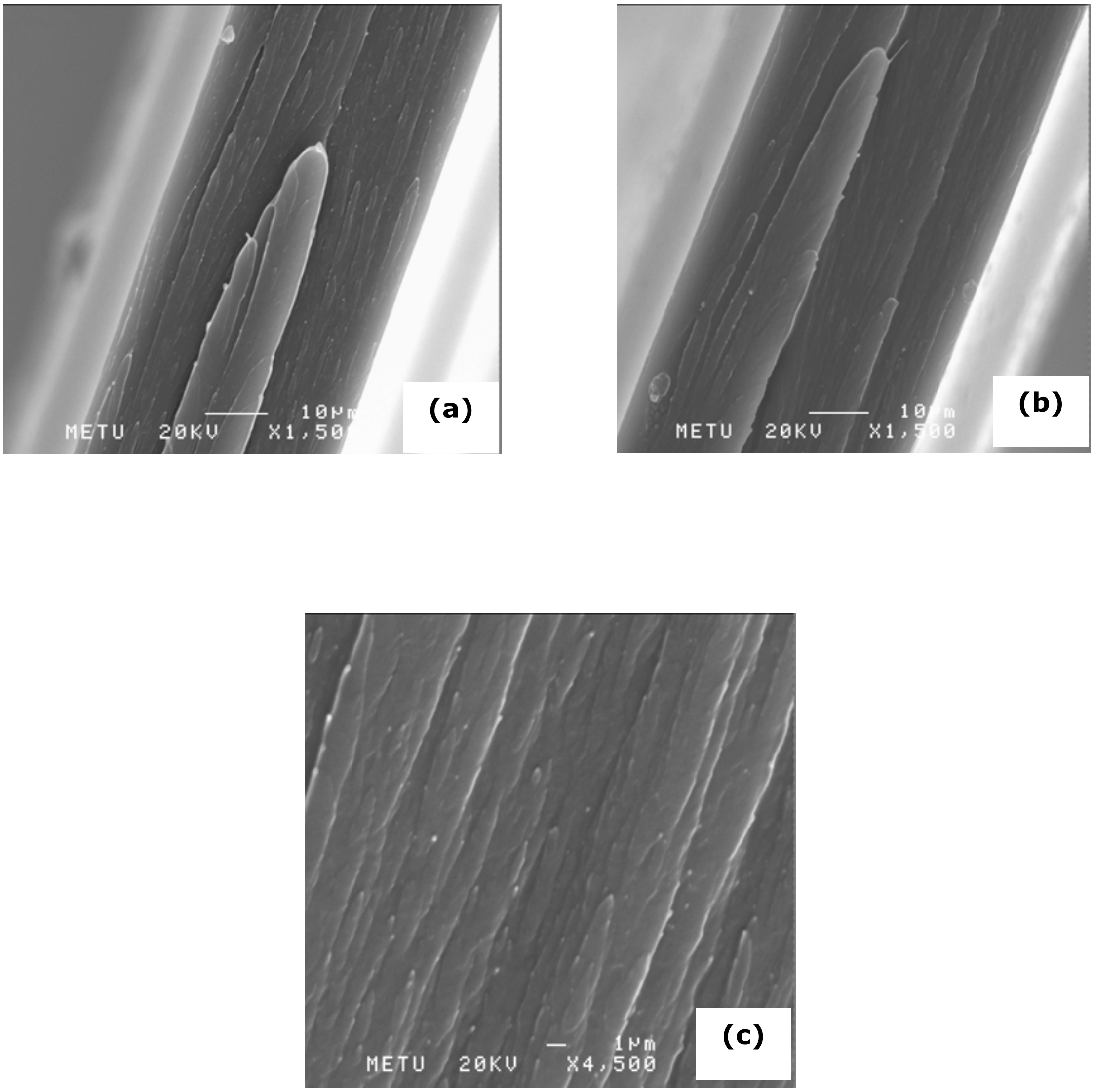


Figure 4.14 SEM micrograph for (a) PC/pNA (1%), (b) PC/ANP (1%), (c) PC/Catechol (1%) membrane.

In conclusion, complete blending of PC with the compatibilizers were observed with the SEM images except for the membrane with 10 w% pNA concentration. The membranes had dense structures and uniform thickness. Thicknesses of the membranes were between 40-60 μm.

4.4.2 TGA Experiments

A solvent residue in the resulting membrane matrix is not desired since it may interact with the membrane matrix and affect the permeation mechanism [54]. In order to investigate whether or not any solvent remained in the membrane after evaporation membranes were analyzed by TGA. Thermograms of the samples were taken in the temperature range of 30-400 °C in N_2 atmosphere at a heating rate of 5 °C/min. A thermogram for PC/pNA blend membrane was given in Figure 4.15.

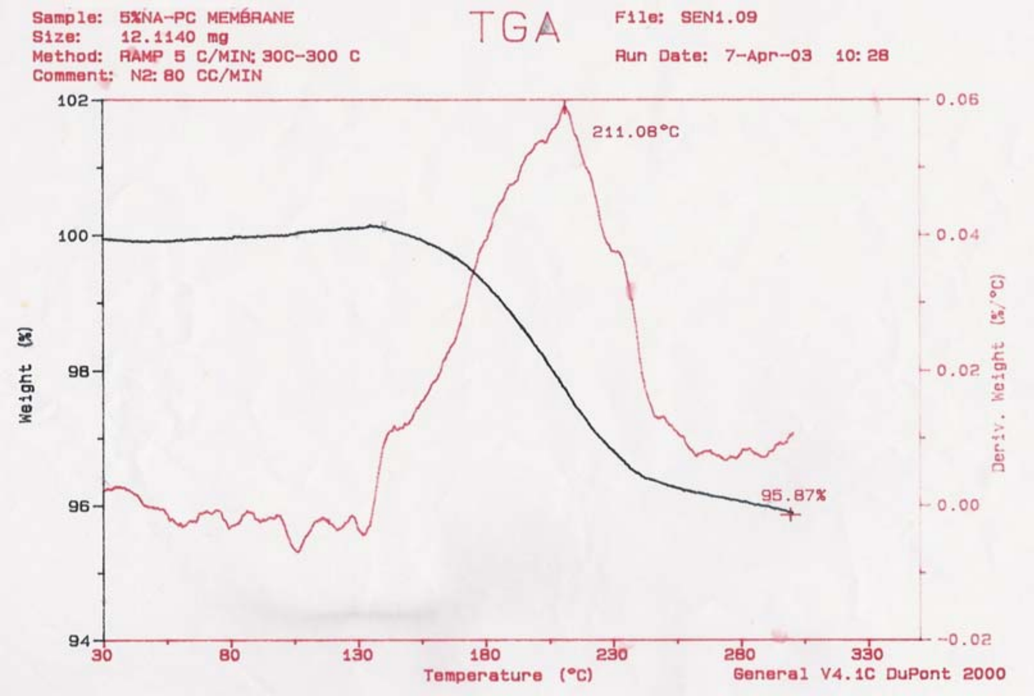


Figure 4.15 TGA graph of pNA/PC (5 w/w%) membrane

The sample lost 5 % of its weight approximately between 130-240 °C. The solvent used in the study was DCM and it has a boiling point of 40 °C. Therefore, there was no solvent loss in the sample in the examined temperature range. This implies that our samples can be considered as solvent free.

4.4.3 DSC Experiments

One of the most important property of a polymeric material is its glass transition temperature. The glass transition temperature (T_g) provides an indirect measurement of the degree of flexibility of polymeric materials at room temperature; the lower the T_g, the more flexible the material. Polymers which have low T_g, have favorable interaction with the zeolites [11].

In this study, DSC thermograms of the membranes, by blending PC with different type of compatibilizers, were obtained and the glass transition temperatures of them were determined at a heating rate of 5 °C/min in N_2 flow. The samples were heated from room temperature to 250 °C, that is well above the glass transition temperature of pure PC membrane (~ 150 °C). Then, they were cooled to room temperature and heated again to 250 °C in N_2 flow. This second scan thermograms were used in determination of T_g to eliminate the thermal historical effects on sample membranes. The DSC thermograms of these membranes were given in Appendix C.

DSC thermograms of PC/pNA blend membranes containing different concentrations of pNA were given in Figure 4.16. T_g of the membranes decreased with increasing pNA concentration and a single glass transition temperature was observed for each membrane. These indicate a change in the structure of polycarbonate with the addition of pNA and the formation of a single phase compatible blend.

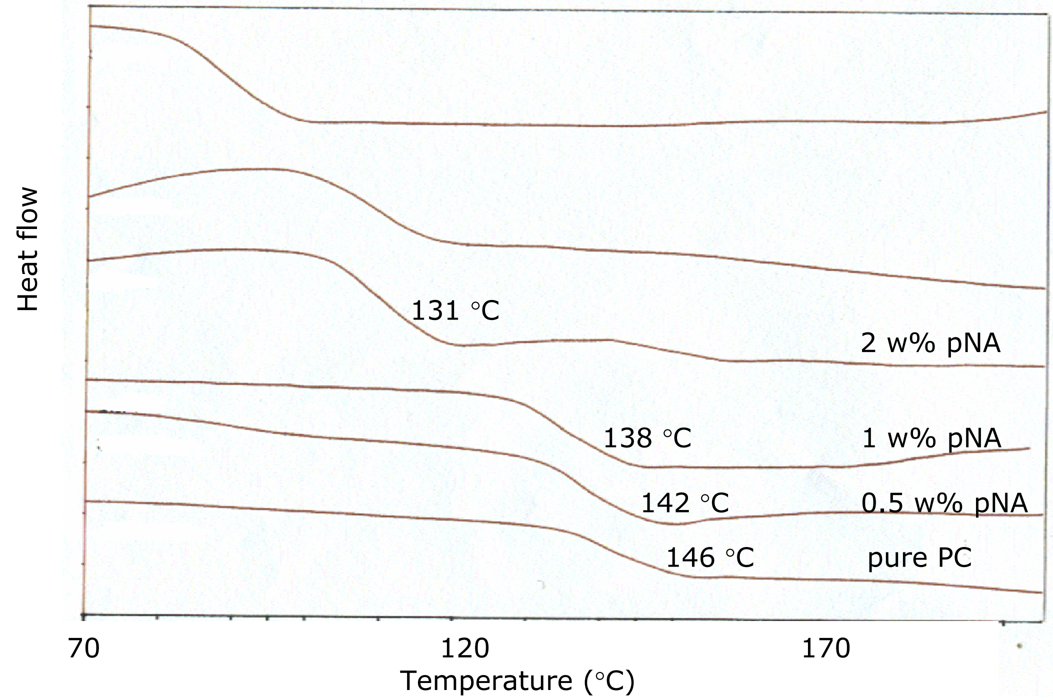


Figure 4.16 DSC graphs of pure PC and PC/pNA membranes

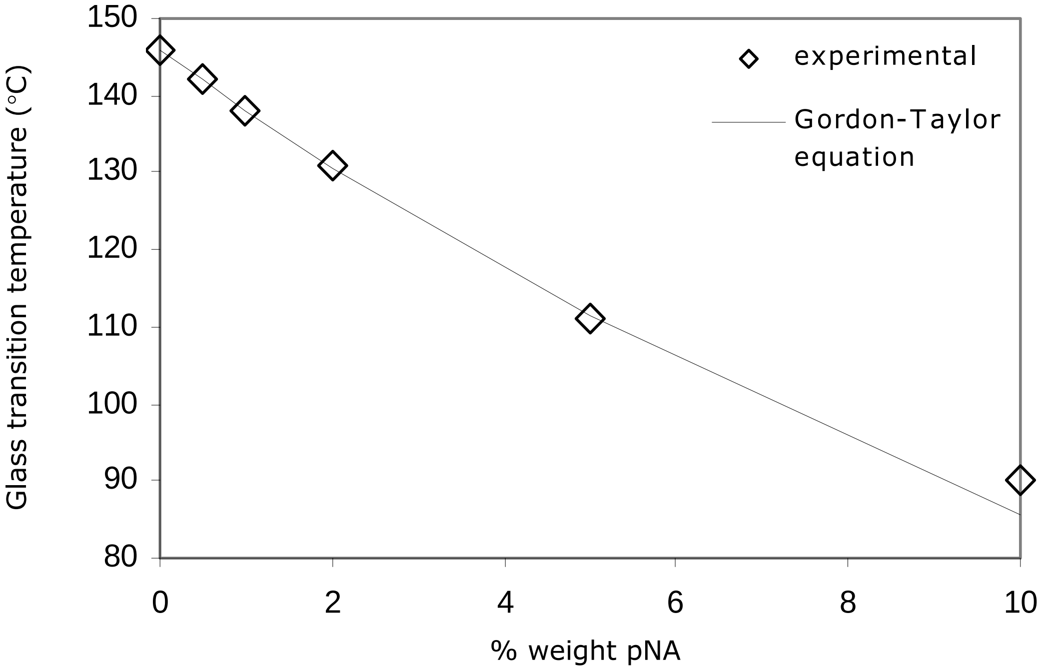


Figure 4.17 Effect of pNA concentration on glass transition temperature

The glass transition temperature of the membranes versus pNA concentration was drawn in Figure 4.17. Glass transition temperature drops with increasing pNA content. The effect of pNA on the T_g of membranes is similar to the effect of LMWCs on glassy polymers [11]. The addition of different types of naphthalenes, phthalates and sebacates, at moderate concentrations (10-30 w%) into glassy polymer matrices decreased the glass transition temperature of polymer significantly. This observation was explained as a diluent effect of these compounds on the polymer matrix. Low glass transition temperature of these additives compared to polymers reduces the glass transition temperature of the resultant material [30, 31]. Although the concentration of pNA in the membrane was very low in this study compared to the concentration of additives in other studies, the resultant effect of pNA on the matrix was similar to them.

Ruiz-Treviňo et al. [15] used the Gordon-Taylor equation to determine the T_g of polymer/additive mixtures:

$$T_g = \frac{w_d T_{gd} + K w_p T_{gp}}{w_d + K w_p}$$

In this equation, T_{gd} and T_{gp} are the glass transition temperatures of the additive and the polymer, respectively. The weight fractions are shown by w_i and K is an adjustable parameter which depends on the type of polymer and additive used and is concentration independent. According to this equation compounds with low T_g decreases the glass transition temperature of polymer (diluent effect). The same formula was applied to our PC/pNA system to determine the T_g of pNA and the adjustable parameter K. For this purpose, the glass transition temperatures of PC/pNA blend membranes, except the membrane with 10 w% pNA, were used. This calculation is shown in Appendix D. The T_g of pNA was found as -34.5 °C and the adjustable parameter, K, was determined as 0.221. Those numbers were then used to calculate the glass transtion temperature of membrane at different pNA concentrations by Gordon-Taylor equation, shown in Figure 4.17. The T_g of 10 w% pNA added membrane deviated from the Gordon-Taylor model. This may be attributed to the non-homogenous dispersion of pNA in the matrix. Indeed, small pNA agglomerates had been observed both visually and by SEM which are probably formed during the evaporation of the solvent in membrane preparation due to low solubility of pNA in DCM at high concentrations. Therefore, the composition of homogenous part of the membrane can be lower than 10 w% pNA concentration, showing that 10 w% exceeds the maximum possible blend composition.

Membranes prepared with ANP, Catechol and HMA at a constant compatibilizer/PC ratio of 1 w/w% were also characterized by DSC experiments. The same procedure was applied and the glass transition temperatures were measured during the second scan by DSC. The DSC graphs were given in Appendix C and the measured glass transition temperatures were shown in Table 4.7. Catechol, among all compatibilizers, exhibited the greatest effect on the T_g of the membrane. The glass transition temperature of the other blend membranes was very similar.

Table 4.7 T_g of PC membranes prepared with different compatibilizers

Membrane	**Tg (^{0}C)**
pure PC	146
PC/ANP (1 w%)	140
PC/pNA (1 w%)	138
PC/HMA (1 w%)	136
PC/Catechol (1 w%)	130

All compatibilizers decreased the glass transition temperature of PC although the concentration of the compatibilizers in the membrane matrix was very low. This might be explained by the diluent effect of compatibilizers on the PC membrane matrix. The compatibilizers that have very low glass transition temperatures diluted the polycarbonate matrix, and decreased the glass transition temperature of the membranes. In addition to this diluent effect, possible interaction between PC and compatibilizer might cause this reduction in T_g. The compatibilizer, such as pNA, lowers the T_g of polycarbonate and thus increases the flexibility of membrane. This is a desired property in preparation of void free MMMs because Mahajan et al. [11] claimed that flexible membranes obtained by adding plasticizers result in good adhesion between the polymer and zeolite particles.

4.4.4 FTIR Experiments

The decreasing tendency of permeabilities with the addition of compatibilizers and the reductions in glass transition temperatures indicates an interaction between PC and compatibilizers, pNA, ANP, HMA and Catechol. Therefore, the membranes were characterized by FTIR. Membranes were analyzed in the film form and compatibilizers were shaped into the pellet form for analysis. Pellets were prepared by mixing compatibilizer with potassium bromide salt. Measurements were performed against air in the mid-infrared region.

FTIR spectra of pure PC membrane and pure pNA powder were given in Figures 4.18 and 4.19, respectively. The characteristics bands observed for PC and pNA were indicated in Table 4.8. Type of vibration and characteristic frequency ranges were also given in this table. The FTIR spectra of PC (Figure 4.18) showed carbonyl stretching peak at 1793-1760 cm^{-1}. It also

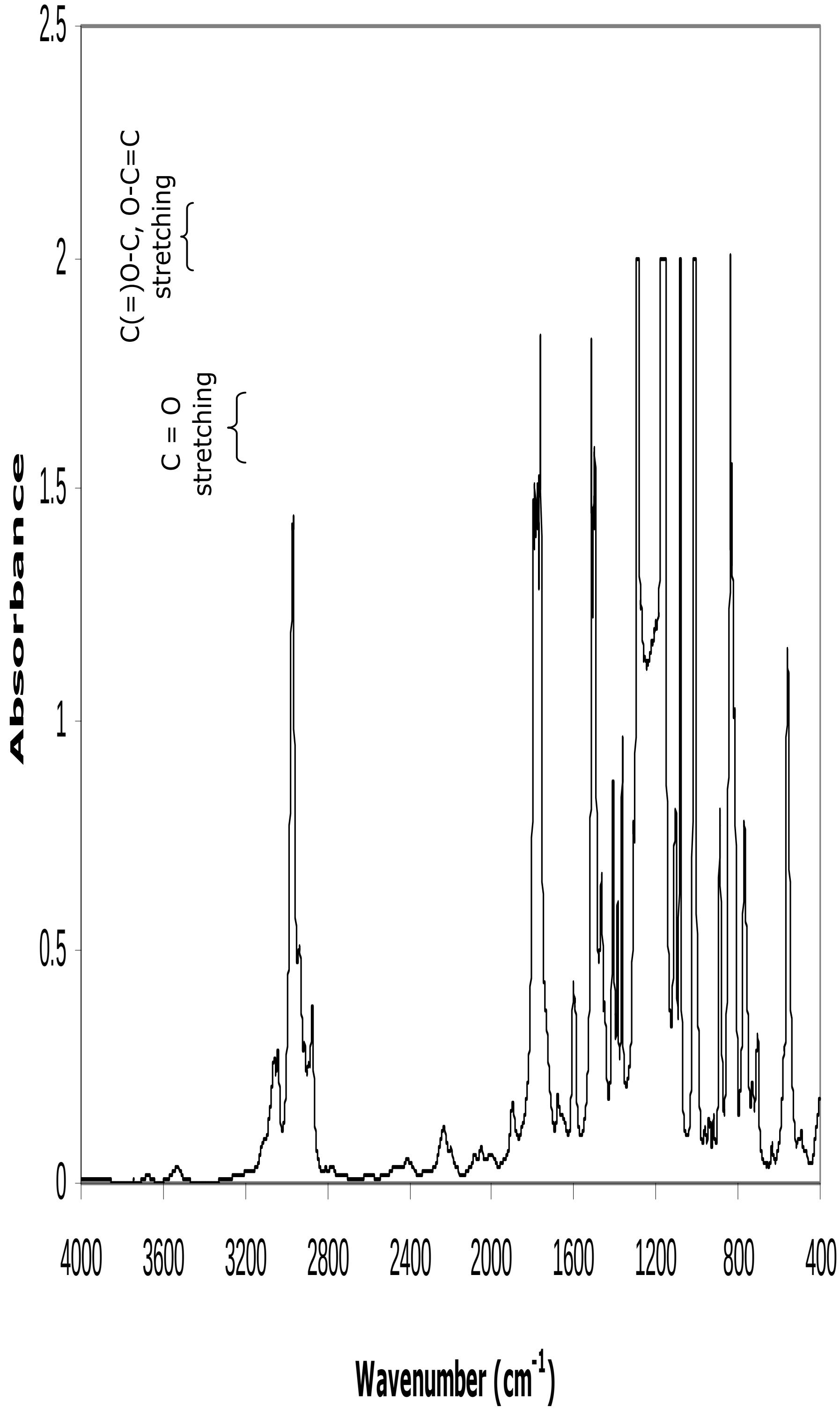


Figure 4.18 FTIR spectra of pure PC membrane

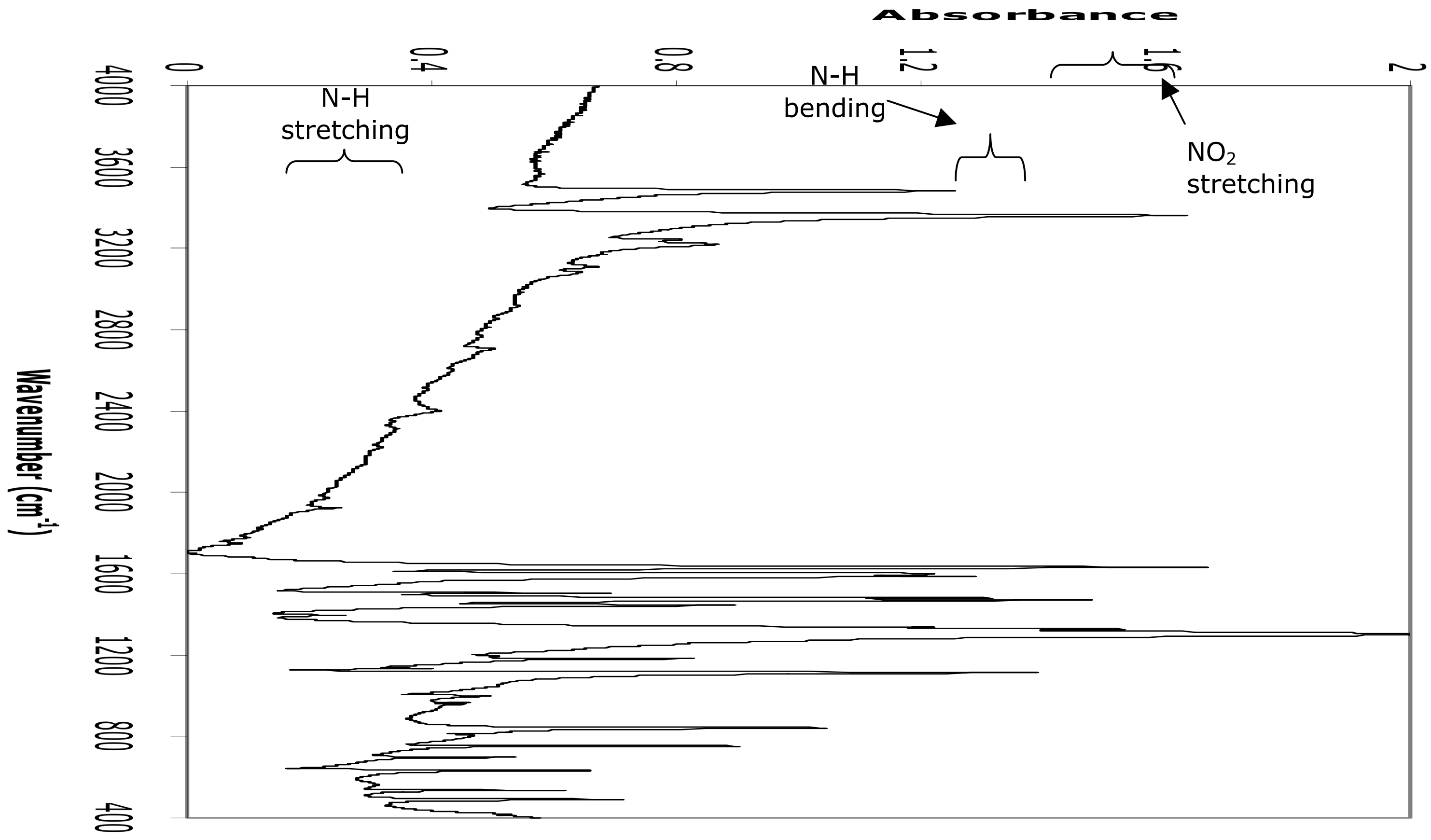


Figure 4.19 FTIR spectra of pure pNA powder (KBr pellet)

Table 4.8 Characteristics FTIR bands of PC and pNA

Pure PC membrane (Figure 4.18)	pNA powder (Figure 4.19)	Type of vibration	Characteristic frequencies (cm^{-1})
	3481 3360	N – H stretching	3500 -3300
3035 2966 2871		C – H stretching	3200 -2800
1793 - 1760		C = O stretching	1820 -1680
	1631 1598 1587	N – H bending	1650 -1580
1280 1215		C(=O)-O stretching O –C=C as. stretching	1300 -1000
	1481 1470 1308	NO_2 stretching	1550 -1500 1360 - 1290
	1336.6 1327 1300	C - NH_2 stretching	1342 - 1266

revealed two characteristics bands of absorption one at 1280 cm^{-1} belonging to C(=O)-O stretching and one at 1215 cm^{-1} belonging to O-C=C stretching. The FTIR spectra of pNA (Figure 4.19) give nitro and amine stretching peaks in the range of 1550-1500 cm^{-1}, 1360-1290 cm^{-1} and 3500-3300 cm^{-1}, respectively.

FTIR spectra of membranes containing different concentrations of pNA were given in Figure 4.20. The amine stretching peaks of pNA could not be seen up to 2 w% of pNA concentration. At this concentration it appeared and shifted from its original position to the high frequency side of the spectra. Similarly amine bending peaks of pNA could not be observed up to 2 w% pNA. After this pNA concentration they started to appear as smaller peaks whose positions shifted to the low frequency side of the spectra.

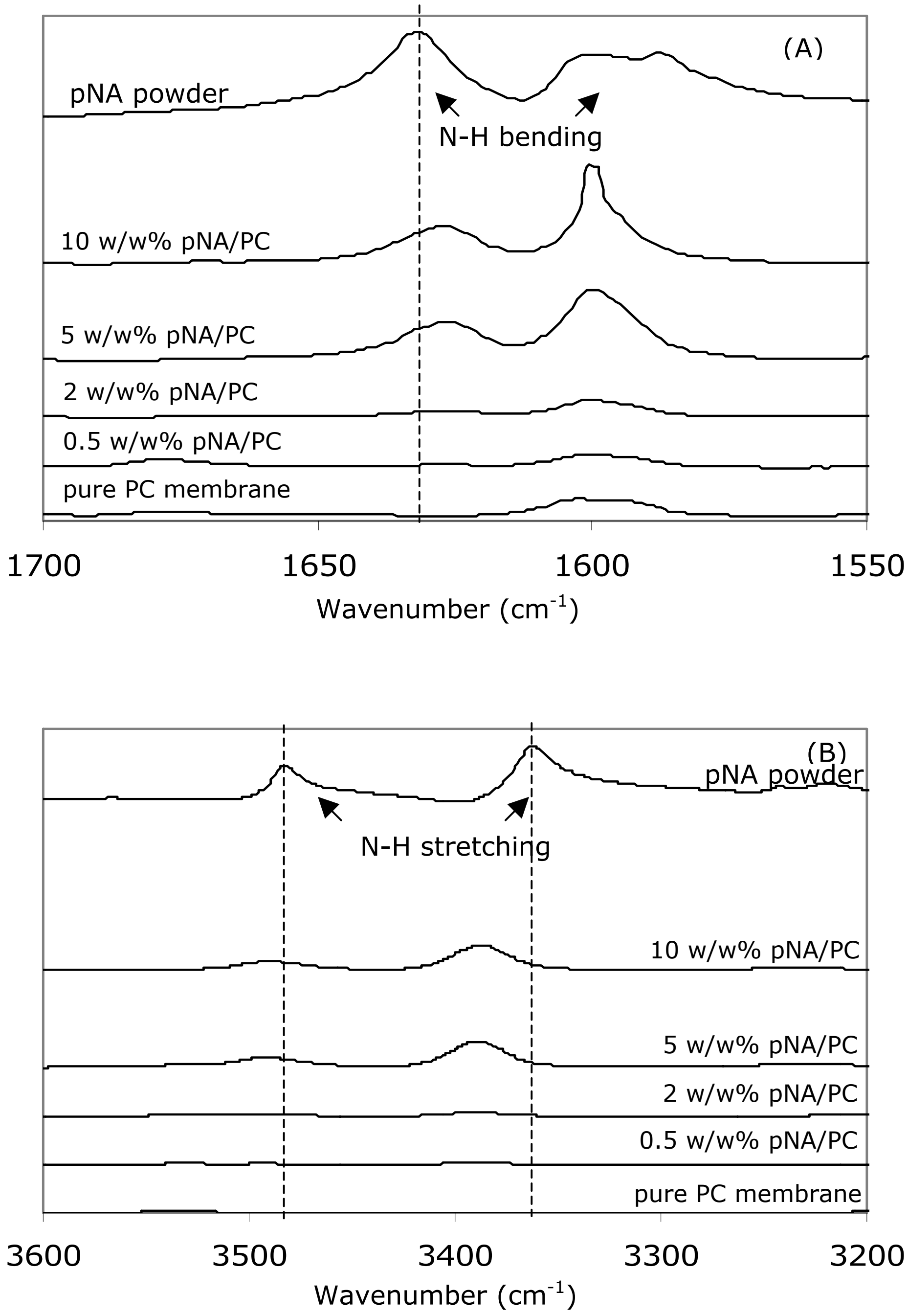


Figure 4.20 FTIR spectra of pure PC, pNA powder and pNA added membranes

The NO_2 stretching bands of pNA could not be observed clearly because of being underneath of the peaks of PC. The shifting of amine peaks of pNA with increasing concentration might indicate an interaction between PC and pNA.

In the study of preparation of mixed matrix membranes with 2,4,6-triaminopyrimidine (TAP) similar shifts in amine stretching and bending bands were observed [14]. They claimed that these shifts indicate a hydrogen bond formation between the carbonyl group of polyimide and the amine group of TAP. They also observed shifts in carbonyl group of polyimide.

The spectra of the pure compatibilizers, ANP, HMA and Catechol were illustrated in Appendix E. They have characteristics bands of –OH stretching in the region of 3550-3200 cm^{-1}. FTIR spectra of the membranes prepared with ANP, Catechol and HMA were also presented in Appendix E. The –OH and –NO_2 stretching bands of these compatibilizers, which appear at 3371 cm^{-1} and 1330 cm^{-1}, respectively, shifted from their original position. The –OH bands are broadened and shifted to the low frequency side of spectrum probably due to intra and intermolecular hydrogen bonding within and between the molecule's functional groups [55]. This effect was mostly pronounced in Catechol, which has two hydroxyl groups.

As a result of observation of shifting and broadening in the amine group of pNA and hydroxyl groups of ANP, HMA and Catechol, existence of an interaction between these groups and polycarbonate can be deduced. The intramolecular hydrogen bonding is also probable between the functional groups of compatibilizer molecules.

4.5 Combination of Gas Separation Performance with Membrane Characterization

PC/compatibilizer membranes prepared in this study were single phase dense polymeric blends as observed in SEM images. Only the membrane blend with 10 w% pNA compatibilizer concentration was non-homogeneous indicating that the maximum possible blend composition was exceeded. All compatibilizer/ polycarbonate blend membranes were permselective. The blend membranes had lower permeability but higher selectivity than pure PC membrane.

The compatibilizers, pNA, ANP, HMA and Catechol acted as antiplasticizers from the membrane performance point of view. They decreased permeability and increased the selectivity of membranes. It was important to note that this antiplasticization effect was provided with very low concentration of compatibilizers in this study, compared to other antiplasticization studies. In addition to that, all compatibilizers decreased the T_g of PC membranes. The highest decrease observed in T_g corresponded to lowest permeability reduction and lowest selectivity increase indicating lowest antiplasticization effect (i.e PC/Catechol blend membrane). Antiplasticization cause stiffenning in membrane and this is the reason of lowest permeability. It must also be stated that the decrease in T_g causes increase in flexibility of polymer. This is a desired property in preparation of void free MMMs. This may occur by good adhesion of polymer to zeolite [11].

The decrease in permeability with the addition of compatibilizer and the reduction in glass transition temperature indicated an interaction between PC and compatibilizers. This interaction was also apparent in FTIR spectra of membranes. It is important that this interaction took place with small concentration of compatibilizer.

Although the compatibilizers had different chemical structure, they all had similar effect on the performance of PC membrane by decreasing the permeabilities and increasing the selectivities. When the chemical structure of compatibilizers are very different like pNA and Catechol, membrane performances and measured glass transition temperatures indicated same differences. pNA contains amine and nitro groups while Catechol contains only hydroxyl groups. Compatibilizer's chemical structure was also effective when the permeate gases was largest like N_2 or smallest like H_2. H_2/N_2 selectivity of PC membranes increased from 42.6 to 82.8 with the addition of 1 w% pNA while it increased only to 68.3 with the addition of 1 w% Catechol.

In conclusion, some criteria on selection of compatibilizer may be suggested. The most important one is that the compatibilizer must interact with PC. Compatibilizers should indicate an antiplasticization effect when it is added to the PC. Compatibilizer type and concentration determines the stiffness and flexibility of membranes. Catechol caused highest flexibility, pNA caused highest stiffening in PC membrane blends, therefore, they can be good compatibilizer candidates for MMMs preparation with zeolites.

CHAPTER 5

CONCLUSIONS

In this study the effect of compatibilizer type and concentration on the PC membrane performance was investigated.

1- Homogeneous polycarbonate/compatibilizer blend membranes were successfully prepared.

2- Low molecular weight compounds with multifunctional groups were found to be promising for use as compatibilizer even at very low concentrations. The compatibilizer should have interaction capability with the polymer matrix. The compatibilizer type and concentration determines the flexibility and stiffness of the resultant membrane.

3- Although the compatibilizers, pNA, ANP, HMA and Catechol, were at very low concentrations in the membranes, they strongly affected the membrane performance and structure because of their antiplasticization effect. Despite the different chemical structure of the compatibilizers, their effect on the membrane performance was similar.

4- The selectivities of membranes increased considerably but the permeabilities of H_2, CO_2, O_2 and N_2 through the membranes decreased due to antiplasticization effect of pNA. The concentration of compatibilizer determined the degree of antiplasticization so that the permeabilities decreased with increasing concentration of pNA.

5- The antiplasticization effect was mostly evident for large non-interacting molecules, like nitrogen.

6- The compatibilizers decreased the glass transition temperature of membrane. The highest decrease was observed for PC/Catechol blend membrane. This matches with the permeability measurements, since the lowest decrease in gas permeations was observed for PC/Catechol blend membrane.

7- The flexibility of PC membrane was increased with addition of compatibilizers, showed by decrease in glass transition temperatures of blend membranes.

8- The shifting and broadening in the amine group of pNA and hydroxyl group of ANP, HMA and Catechol in the FTIR spectra of PC/compatibilizer membranes indicated an interaction between PC and compatibilizers.

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APPENDIX A

DETERMINATION OF PERMEABILITIES OF GASES

A.1 Permeability calculation

Pressure change with respect to time data points were taken with certain time intervals. This time intervals were changed with respect to gases used. For fast gases, hydrogen, oxygen and carbondioxide this interval was in the range of 10-30 seconds; for slow gas nitrogen this interval was 60-120 seconds. In Figure A.1 pressure vs. time graphs of hydrogen was illustrated. From the slope of this graph permeability was calculated according to the algorithm given in Figure A.2.

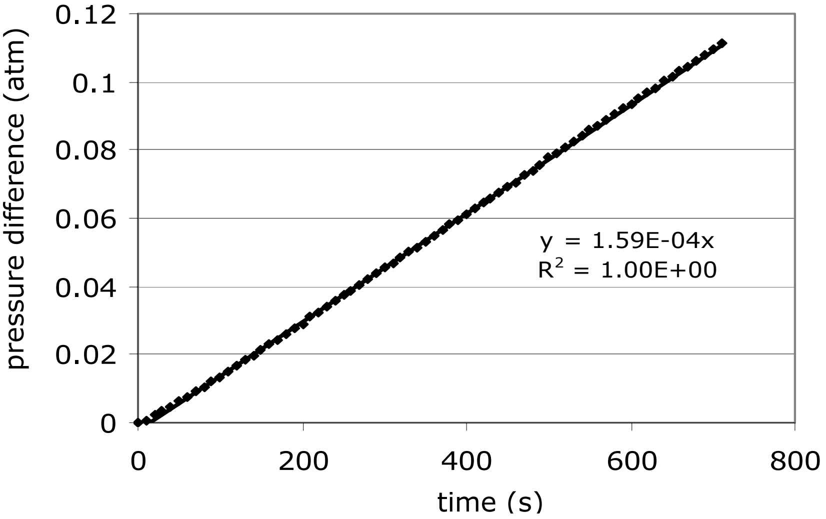


Figure A.1 Pressure difference vs. time graph for H_2 through pure PC membrane

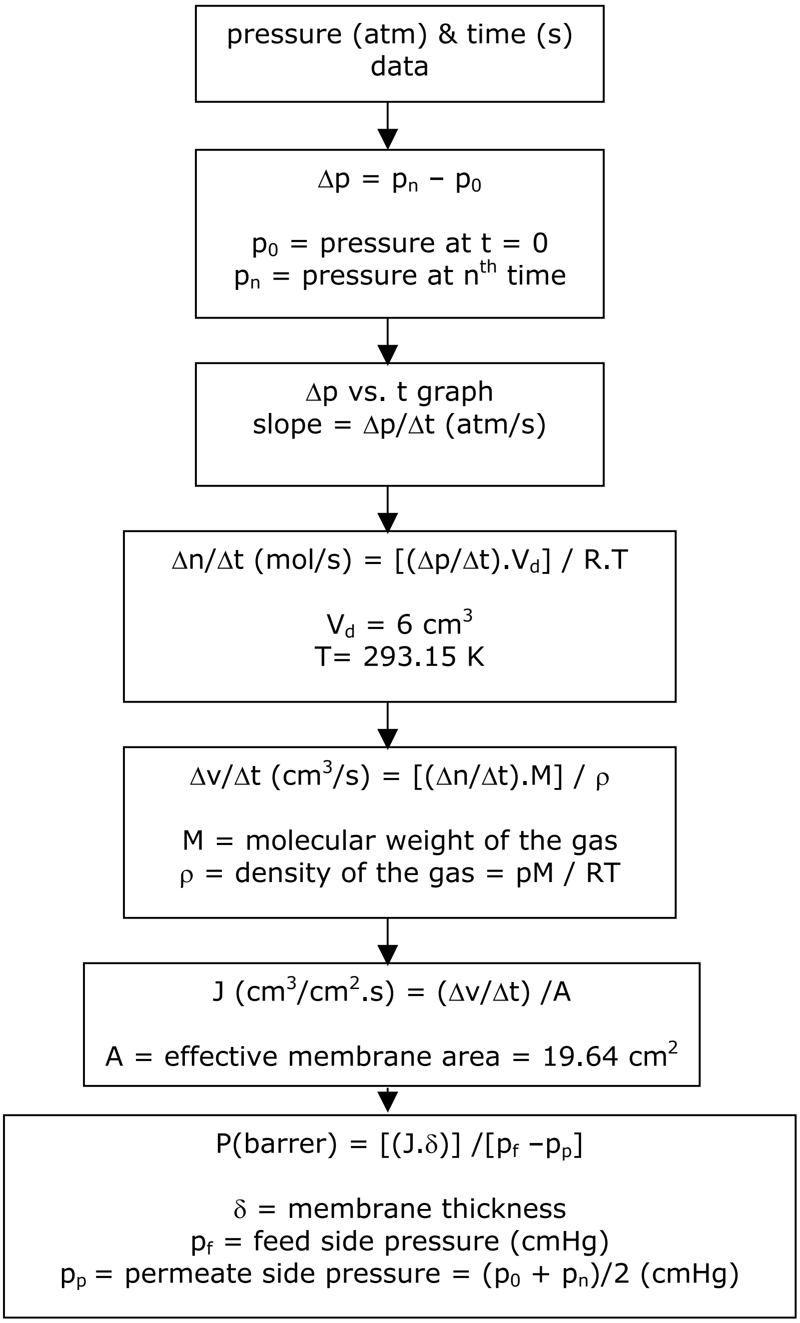


Figure A.2 Algorithm for permeability calculation

A.2 The change of permeability during permeability measurement

Permeability change was determined in two ways; for small constant time intervals and for small constant pressure intervals. The pressure vs. time data obtained in permeability measurement were used for this purpose. For each time or pressure interval $\Delta p/\Delta t$ was calculated. Then, algorithm given in Appendix A.1 was applied in the same manner to find permeabilities for each interval and average permeability was calculated for whole run. Sample calculations for constant time and pressure interval were given in Table A.2.1

Table A.2.1 A sample calculation of permeability with constant time interval (Δt = 30 s) for H_2

time (s)	P (atm)	Δp (atm.)	Δp/Δt (atm/s)	Δn/Δt (mol/s)	pavg (atm)	Δv/Δt (cm3/s)	J (cm3/cm2.s)	P (barrer)
0	0.837	0.0000	0.000000					
30	0.840	0.0034	0.000114	2.826E-08	0.8386	0.00082	4.154E-05	7.89
60	0.844	0.0041	0.000136	3.369E-08	0.8423	0.00097	4.931E-05	9.38
90	0.849	0.0047	0.000158	3.912E-08	0.8467	0.00112	5.697E-05	10.85
120	0.854	0.0047	0.000158	3.912E-08	0.8514	0.00111	5.665E-05	10.81
150	0.858	0.0043	0.000145	3.586E-08	0.8560	0.00101	5.166E-05	9.87
180	0.863	0.0046	0.000154	3.804E-08	0.8605	0.00107	5.450E-05	10.43
210	0.868	0.0050	0.000167	4.130E-08	0.8653	0.00116	5.885E-05	11.28
240	0.873	0.0049	0.000162	4.021E-08	0.8702	0.00112	5.697E-05	10.94
270	0.877	0.0045	0.000149	3.695E-08	0.8749	0.00102	5.207E-05	10.02
300	0.882	0.0051	0.000171	4.238E-08	0.8797	0.00117	5.940E-05	11.45
330	0.887	0.0046	0.000154	3.804E-08	0.8845	0.00104	5.302E-05	10.24
360	0.892	0.0049	0.000162	4.021E-08	0.8893	0.00109	5.575E-05	10.78
390	0.896	0.0047	0.000158	3.912E-08	0.8941	0.00106	5.395E-05	10.45
420	0.901	0.0047	0.000158	3.912E-08	0.8988	0.00105	5.367E-05	10.42
450	0.906	0.0049	0.000162	4.021E-08	0.9036	0.00108	5.486E-05	10.67
480	0.911	0.0049	0.000162	4.021E-08	0.9085	0.00107	5.457E-05	10.63
510	0.916	0.0050	0.000167	4.130E-08	0.9134	0.00109	5.574E-05	10.88
540	0.921	0.0051	0.000171	4.238E-08	0.9185	0.00112	5.689E-05	11.12
570	0.926	0.0046	0.000154	3.804E-08	0.9234	0.00100	5.079E-05	9.95
600	0.930	0.0047	0.000158	3.912E-08	0.9280	0.00102	5.198E-05	10.20
630	0.935	0.0047	0.000158	3.912E-08	0.9328	0.00102	5.171E-05	10.16
660	0.940	0.0050	0.000167	4.130E-08	0.9376	0.00107	5.430E-05	10.69
690	0.945	0.0047	0.000158	3.912E-08	0.9425	0.00101	5.118E-05	10.40

Table A.2.2 A sample calculation of permeability with constant pressure interval (Δp = 0.003 atm.) for H_2

Time (sec)	P (atm)	Δp (atm.)	Δp/Δt (atm/s)	Δn/Δt (mol/s)	pavg (atm)	Δv/Δt (cm3/s)	J (cm3/cm2.s)	P (barrer)
0	0.837	0.0000						
30	0.840	0.0034	0.000114	2.826E-08	0.8386	0.00082	4.154E-05	7.89
60	0.844	0.0041	0.000136	3.369E-08	0.8423	0.00097	4.931E-05	9.38
90	0.849	0.0047	0.000158	3.912E-08	0.8467	0.00112	5.697E-05	10.85
140	0.857	0.0075	0.000150	3.717E-08	0.8528	0.00106	5.373E-05	10.26
170	0.861	0.0046	0.000154	3.804E-08	0.8589	0.00107	5.460E-05	10.44
190	0.864	0.0033	0.000164	4.075E-08	0.8628	0.00114	5.823E-05	11.15
220	0.869	0.0047	0.000158	3.912E-08	0.8668	0.00109	5.565E-05	10.67
240	0.873	0.0034	0.000171	4.238E-08	0.8709	0.00118	6.000E-05	11.53
260	0.876	0.0030	0.000151	3.749E-08	0.8741	0.00104	5.288E-05	10.17
290	0.881	0.0049	0.000162	4.021E-08	0.8781	0.00111	5.646E-05	10.88
310	0.884	0.0032	0.000158	3.912E-08	0.8821	0.00107	5.468E-05	10.55
340	0.888	0.0047	0.000158	3.912E-08	0.8861	0.00107	5.444E-05	10.52
360	0.892	0.0033	0.000164	4.075E-08	0.8901	0.00111	5.645E-05	10.92
390	0.896	0.0047	0.000158	3.912E-08	0.8941	0.00106	5.395E-05	10.45
410	0.900	0.0034	0.000171	4.238E-08	0.8982	0.00114	5.818E-05	11.29
440	0.904	0.0046	0.000154	3.804E-08	0.9022	0.00102	5.198E-05	10.10
460	0.908	0.0030	0.000151	3.749E-08	0.9060	0.00100	5.102E-05	9.93
490	0.913	0.0051	0.000171	4.238E-08	0.9101	0.00113	5.742E-05	11.19
530	0.919	0.0064	0.000161	3.994E-08	0.9159	0.00106	5.377E-05	10.50
550	0.923	0.0037	0.000184	4.565E-08	0.9209	0.00120	6.111E-05	11.96
580	0.927	0.0046	0.000154	3.804E-08	0.9251	0.00100	5.070E-05	9.94
600	0.930	0.0030	0.000151	3.749E-08	0.9289	0.00098	4.977E-05	9.77
630	0.935	0.0047	0.000158	3.912E-08	0.9328	0.00102	5.171E-05	10.16
650	0.939	0.0034	0.000171	4.238E-08	0.9368	0.00110	5.578E-05	10.98
680	0.943	0.0046	0.000154	3.804E-08	0.9409	0.00098	4.984E-05	9.83

APPENDIX B

REPRODUCIBILITY EXPERIMENTS

B.1 Reproducibility Data for PC/pNA Membranes

Table B.1.1 Reproducibility Data for pNA/PC= 0.5 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
M1 (40 µm)	1	0.174	10.74	1.35	5.59			
	2	0.180	10.81	1.34	5.54			
	avg.	0.177	10.78	1.35	5.57	60.9	7.6	31.5
M2 (45 µm)	1	0.110	10.94	1.31	5.04			
	2	0.120	10.84	1.27	5.00			
	avg.	0.115	10.89	1.29	5.02	94.7	11.2	43.7

Table B.1.2 Reproducibility Data for pNA/PC= 1 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
M1 (40 µm)	1	0.132	10.85	1.22	4.63			
	2	0.127	10.64	1.19	4.59			
	avg.	0.130	10.75	1.21	4.61	82.7	9.3	35.5
M2 (45 µm)	1	0.127	10.83	1.19	4.93			
	2	0.130	10.70	1.22	4.95			
	avg.	0.129	10.77	1.21	4.94	83.5	9.4	38.3

Table B.1.3 Reproducibility Data for pNA/PC= 2 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
M1 (40 µm)	1	0.096	9.40	0.97	3.57			
	2	0.100	9.42	1.00	3.40			
	avg.	0.098	9.41	0.99	3.49	96.0	10.1	35.6
M2 (45 µm)	1	0.099	9.78	0.98	3.66			
	2	0.102	9.82	1.03	3.80			
	avg.	0.101	9.80	1.00	3.73	97.0	9.9	36.9

Table B.1.4 Reproducibility Data for pNA/PC= 5 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
M1 (45 µm)	1	0.065	7.39	0.88	3.49			
	2	0.063	7.27	0.84	3.41			
	avg.	0.064	7.33	0.86	3.45	114.5	13.4	53.9
M2 (40 µm)	1	0.069	7.79	0.83	3.47			
	2	0.067	7.73	0.84	3.45			
	avg.	0.068	7.76	0.84	3.46	114.1	12.4	50.9

Table B.1.5 Reproducibility Data for pNA/PC= 10 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
M1 (45 µm)	1	0.046	5.65	0.37	1.43			
	2	0.041	5.72	0.37	1.37			
	avg.	0.044	5.69	0.37	1.40	129.3	8.4	31.8
M2 (50 µm)	1	0.040	5.17	0.41	1.30			
	2	0.040	5.32	0.40	1.37			
	avg.	0.040	5.25	0.41	1.34	131.3	10.3	33.5

B.2 Reproducibility Data for Other Compatibilizers

Table B.2.1 Reproducibility Data for ANP/PC= 1 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
	1	0.158	11.48	1.44	5.73			
M1	2	0.157	11.54	1.44	5.69			
(55 µm)	avg.	0.161	11.51	1.44	5.71	72.4	9.1	35.9
	1	0.164	11.32	1.45	5.82			
M2	2	0.163	11.23	1.47	5.81			
(50 µm)	avg.	0.164	11.28	1.46	5.82	68.8	8.9	35.5

Table B.2.2 Reproducibility Data for Catechol/PC= 1 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
	1	0.186	12.06	1.56	6.46			
M1	2	0.180	11.98	1.57	6.51			
(50 µm)	avg.	0.183	12.02	1.57	6.49	65.7	8.6	35.5
	1	0.184	12.49	1.67	6.67			
M2	2	0.186	12.60	1.68	6.80			
(50 µm)	avg.	0.185	12.55	1.68	6.74	67.8	9.1	36.4

Table B.2.3 Reproducibility Data for HMA/PC= 1 w/w% Membrane

Membrane Number	Run Number	Permeability (barrer)				Selectivity (X/N_2)		
		N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
	1	0.156	11.92	1.40	6.14			
M1	2	0.152	11.94	1.37	6.12			
(50 µm)	avg.	0.154	11.93	1.39	6.13	77.5	9.0	39.8
	1	0.153	12.15	1.43	6.03			
M2	2	0.156	11.96	1.42	6.10			
(45 µm)	avg.	0.155	12.06	1.43	6.07	77.8	9.2	39.2

APPENDIX C

DIFFERENTIAL SCANNING CALORIMETRY GRAPHS

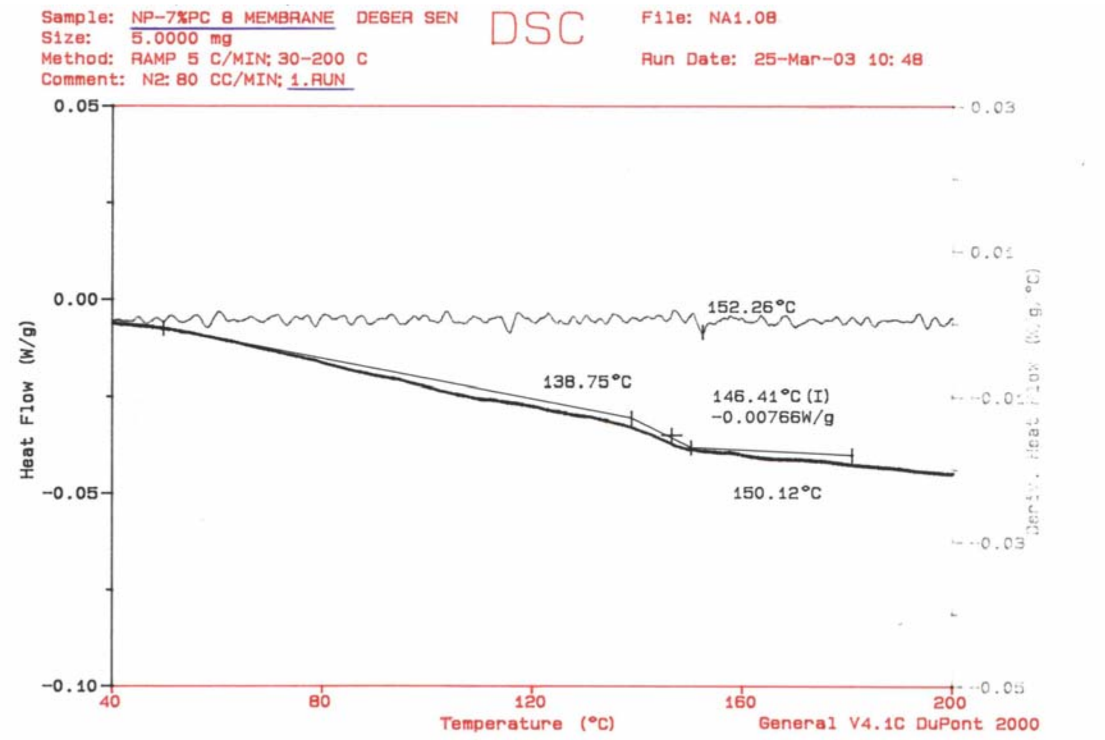


Figure C.1 The DSC graph of pure PC membrane

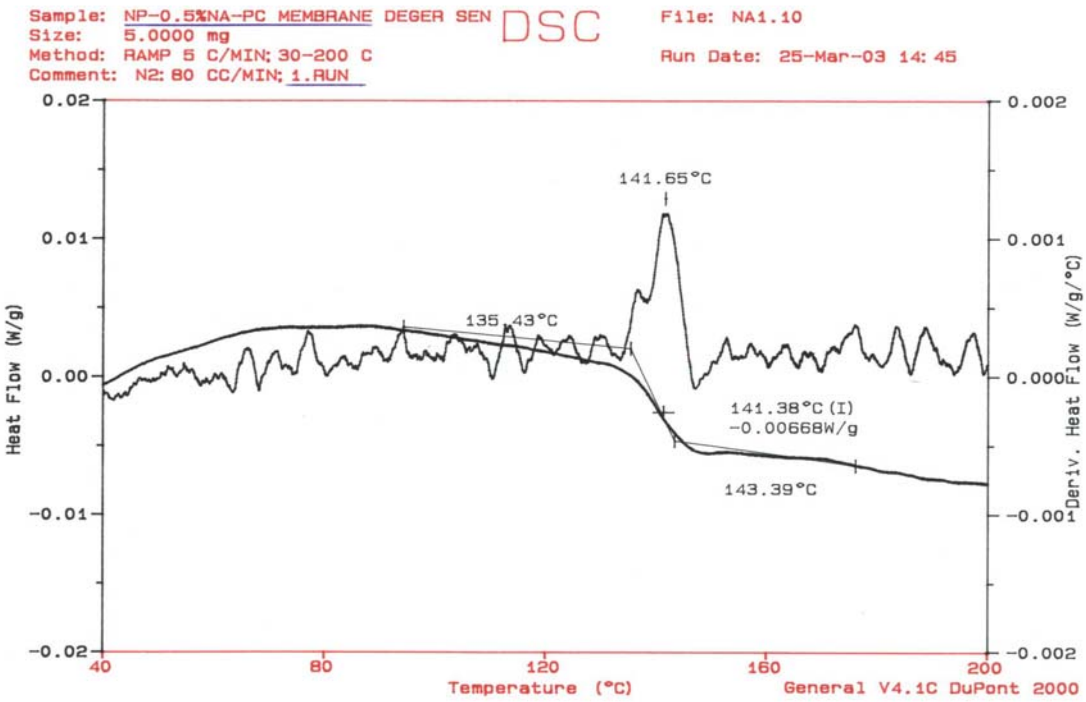


Figure C.2 The DSC graph of pNA/PC (0.5 w/w%) membrane (Run 1)

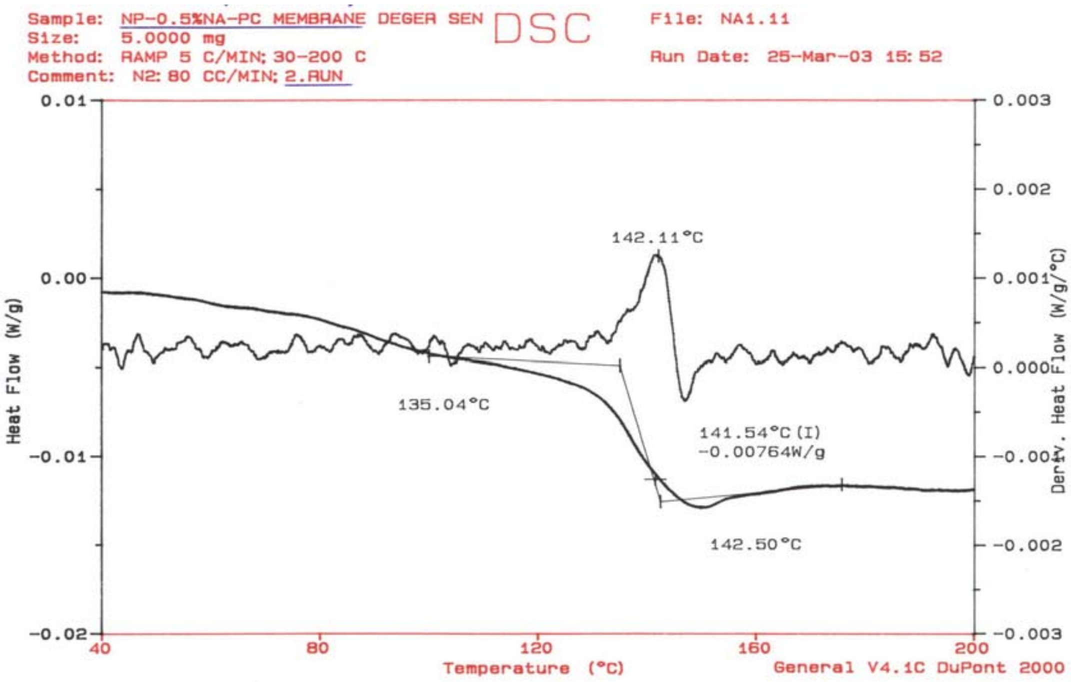


Figure C.3 The DSC graph of pNA/PC (0.5 w/w%) membrane (Run 2)

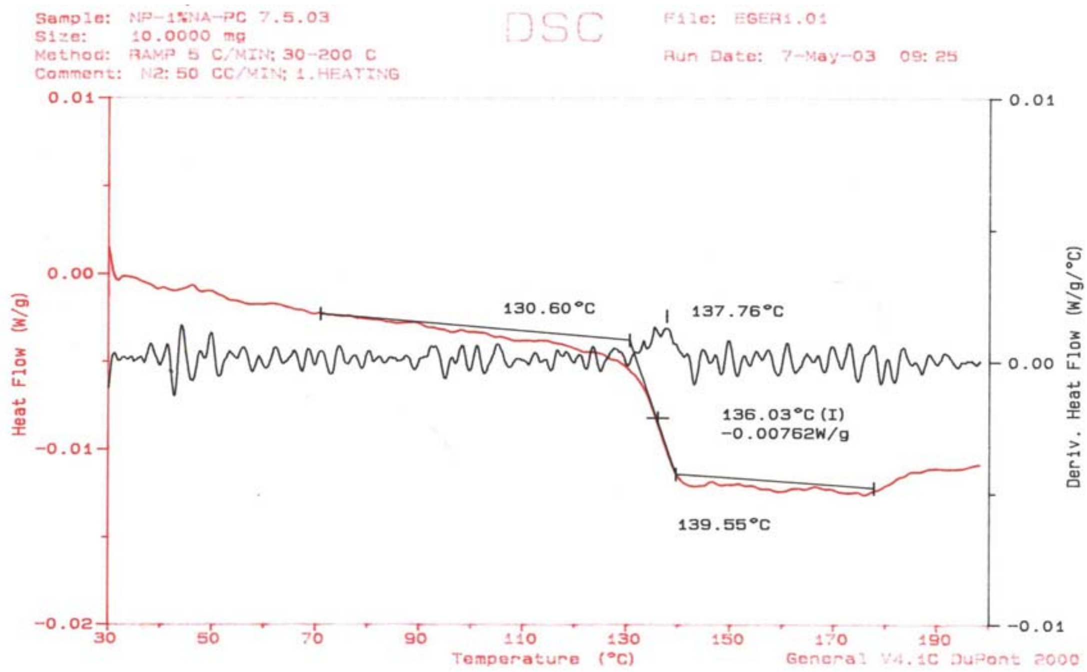


Figure C.4 The DSC graph of pNA/PC (1 w/w%) membrane (Run 1)

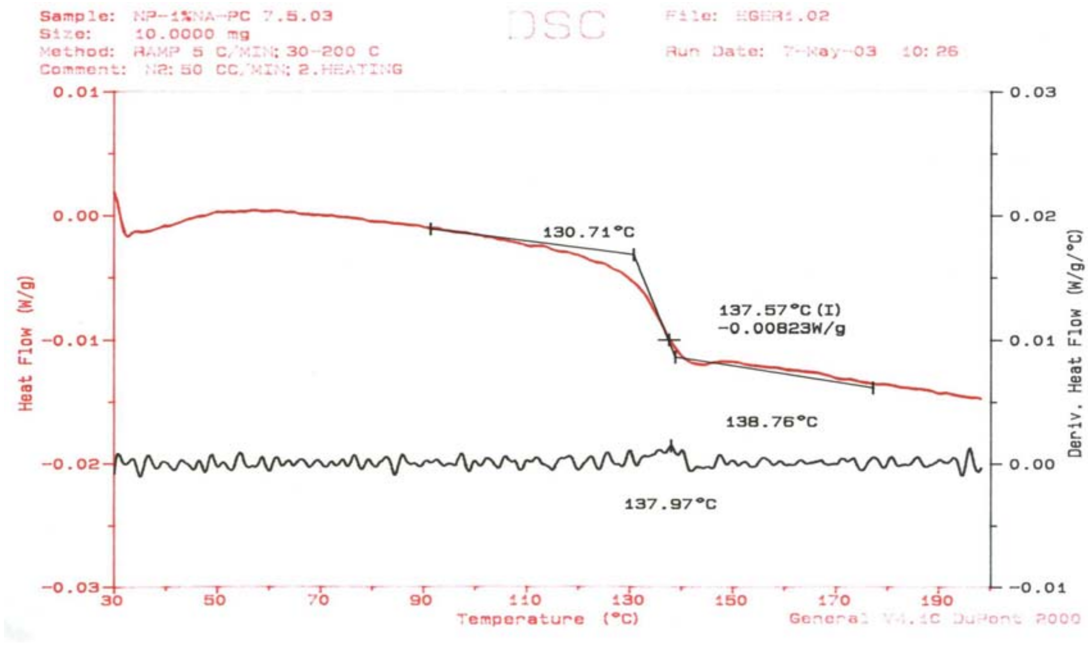


Figure C.5 The DSC graph of pNA/PC (1 w/w%) membrane (Run 2)

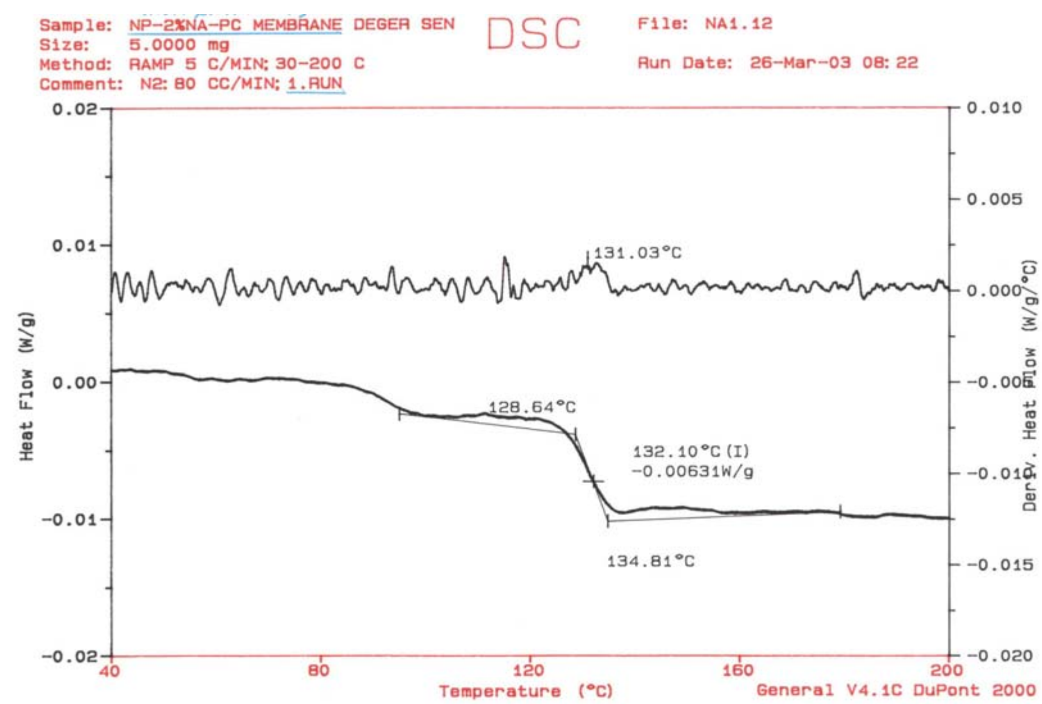


Figure C.6 The DSC graph of pNA/PC (2 w/w%) membrane (Run 1)

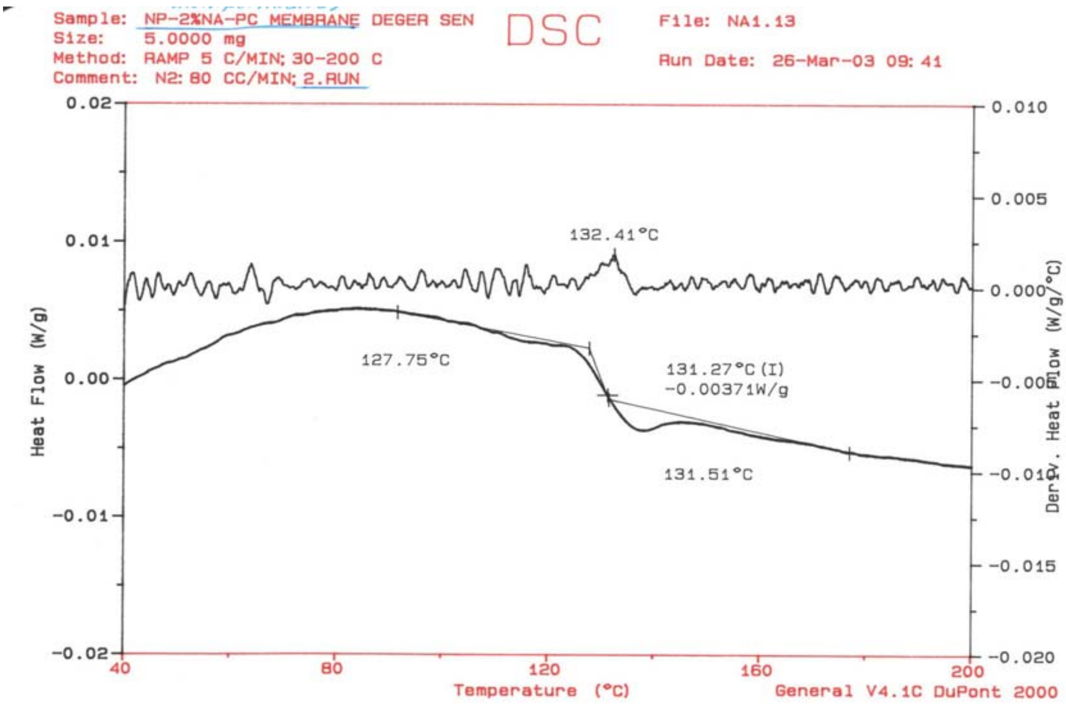


Figure C.7 The DSC graph of pNA/PC (2 w/w%) membrane (Run 2)

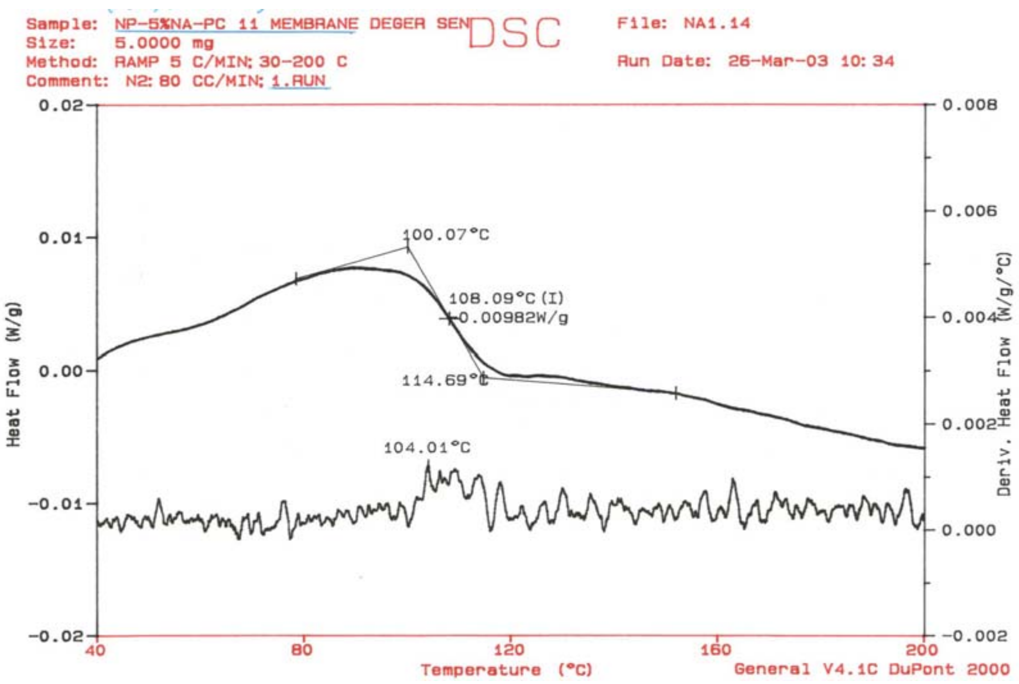


Figure C.8 The DSC graph of pNA/PC (5 w/w%) membrane (Run 1)

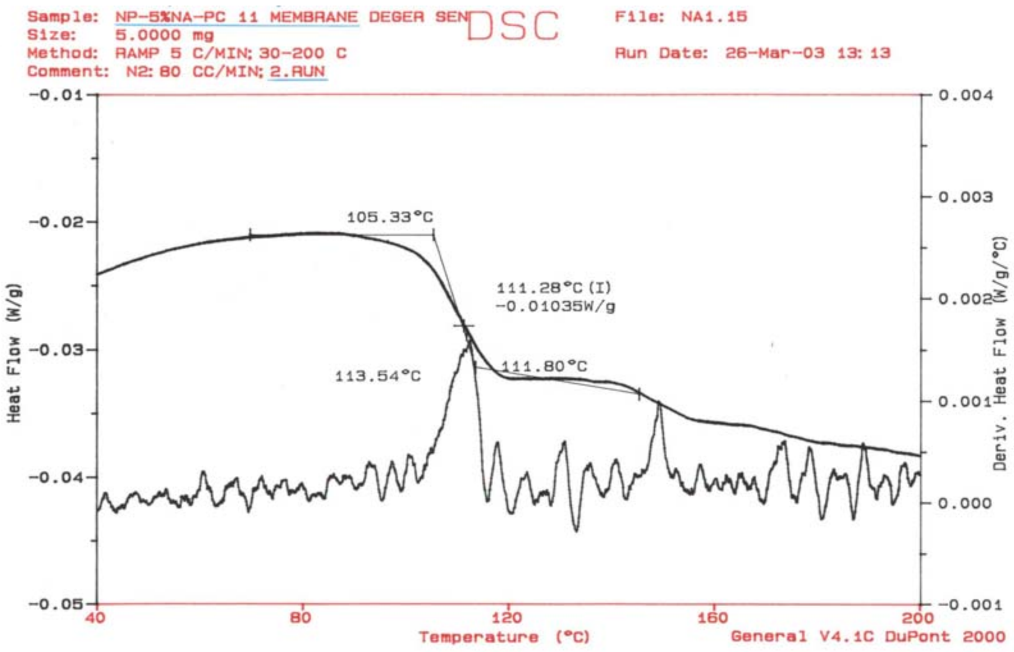


Figure C.9 The DSC graph of pNA/PC (5 w/w%) membrane (Run 2)

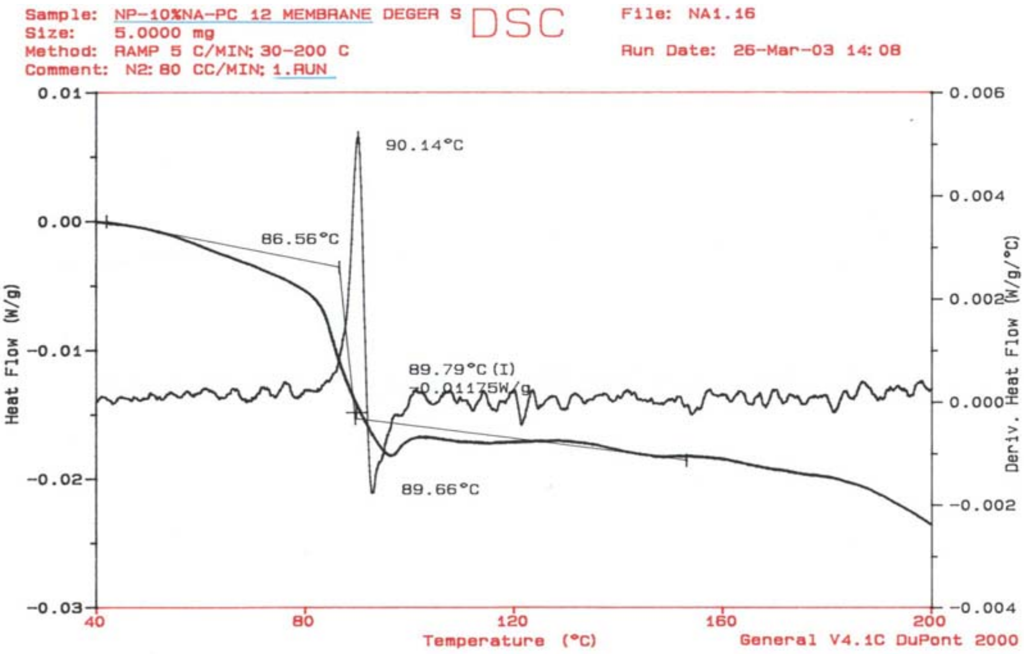


Figure C.10 The DSC graph of pNA/PC (10 w/w%) membrane (Run 1)

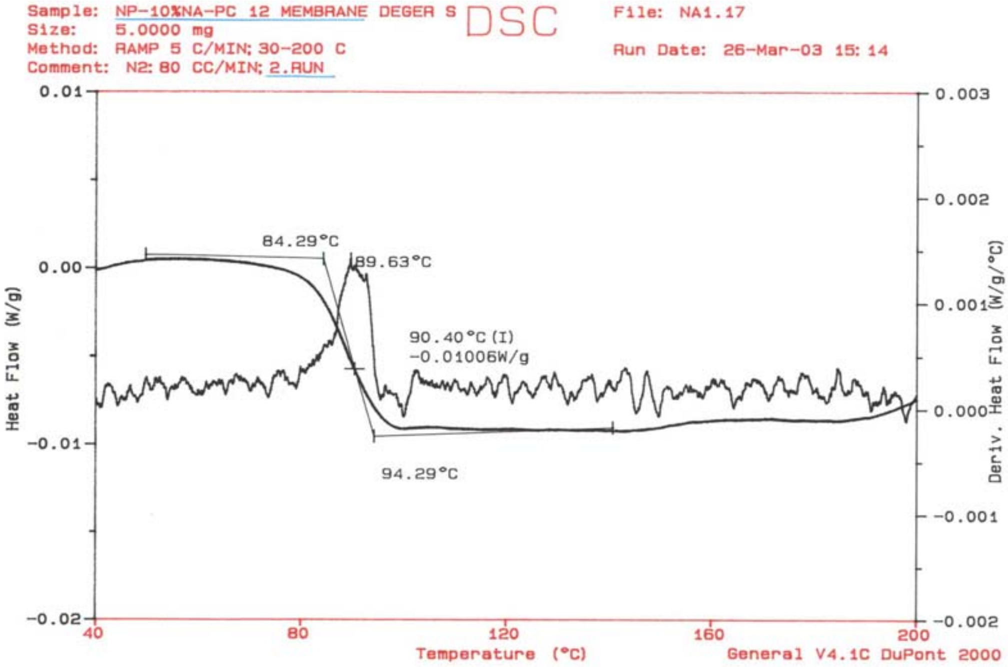


Figure C.11 The DSC graph of pNA/PC (10 w/w%) membrane (Run 2)

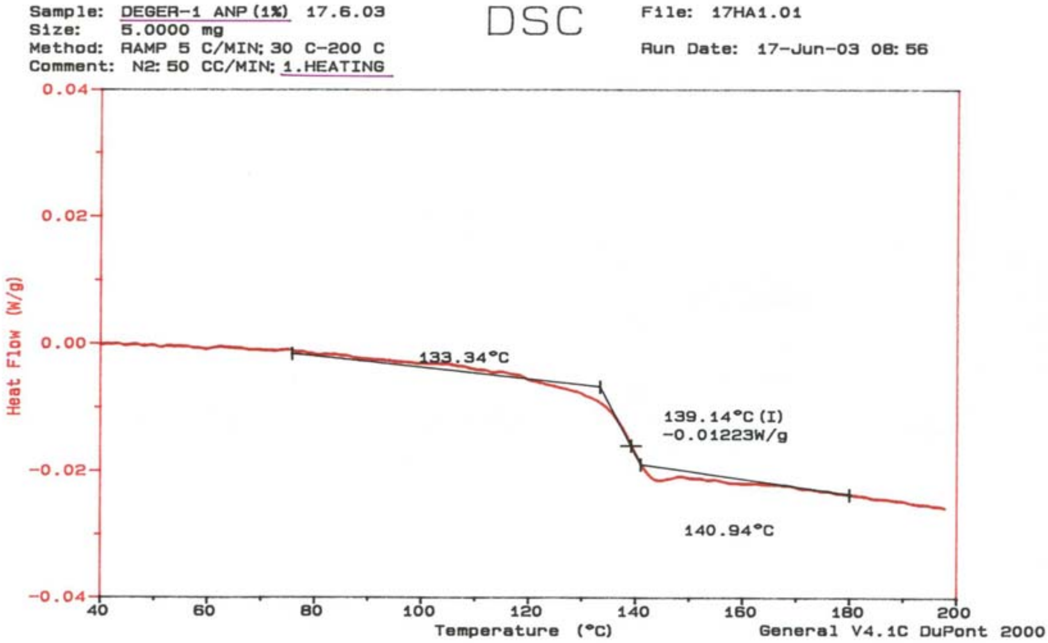


Figure C.12 The DSC graph of ANP/PC (1 w/w%) membrane (Run 1)

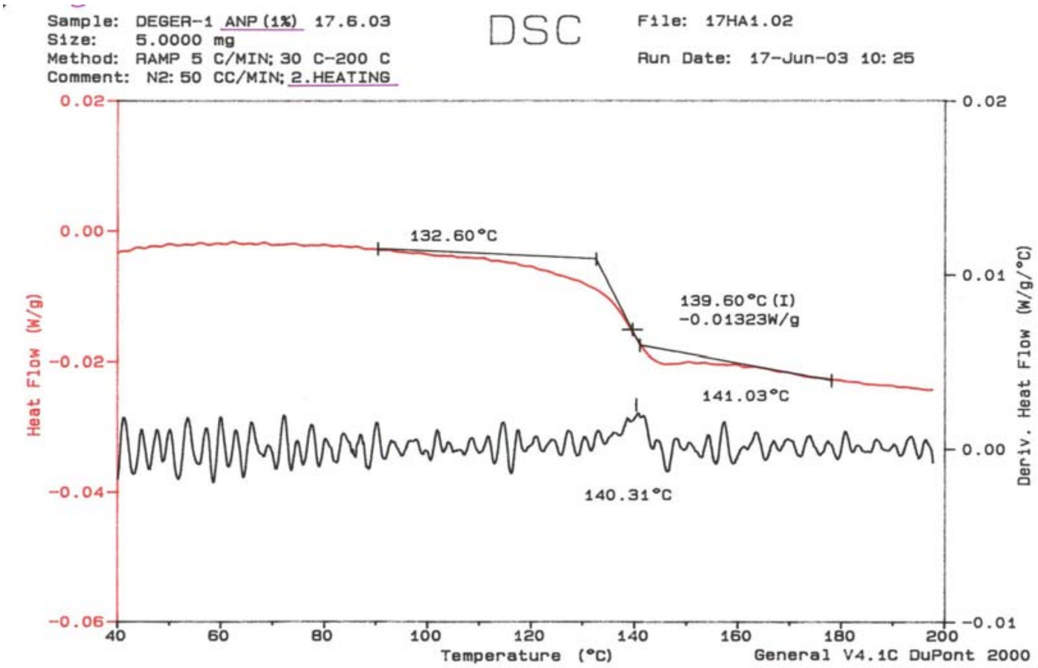


Figure C.13 The DSC graph of ANP/PC (1 w/w%) membrane (Run 2)

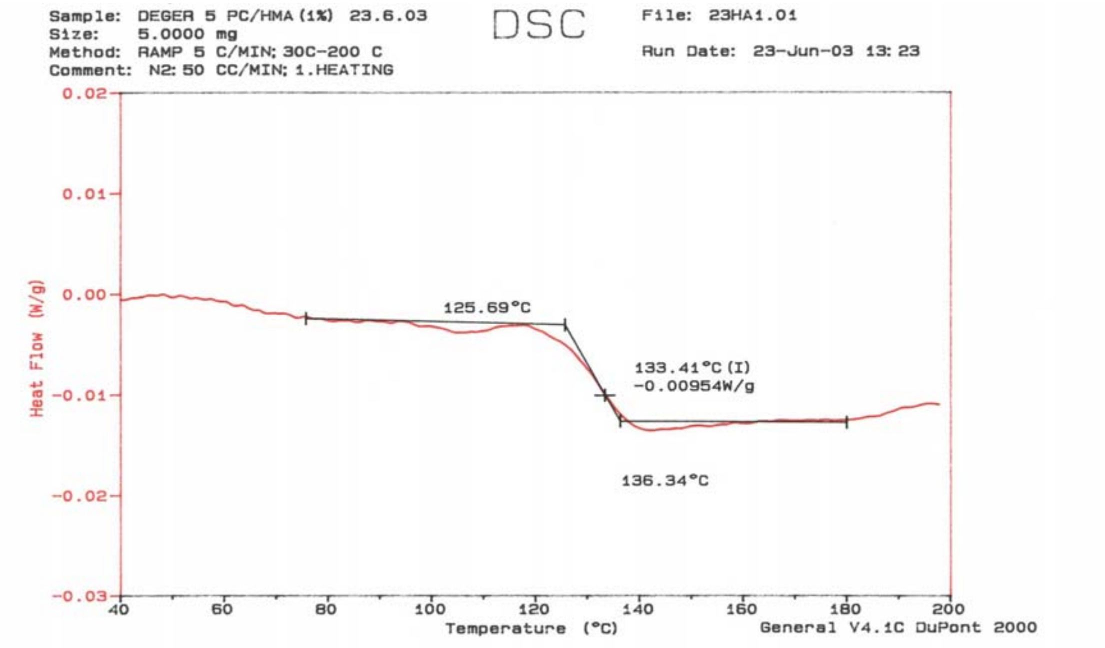


Figure C.14 The DSC graph of HMA/PC (1 w/w%) membrane (Run 1)

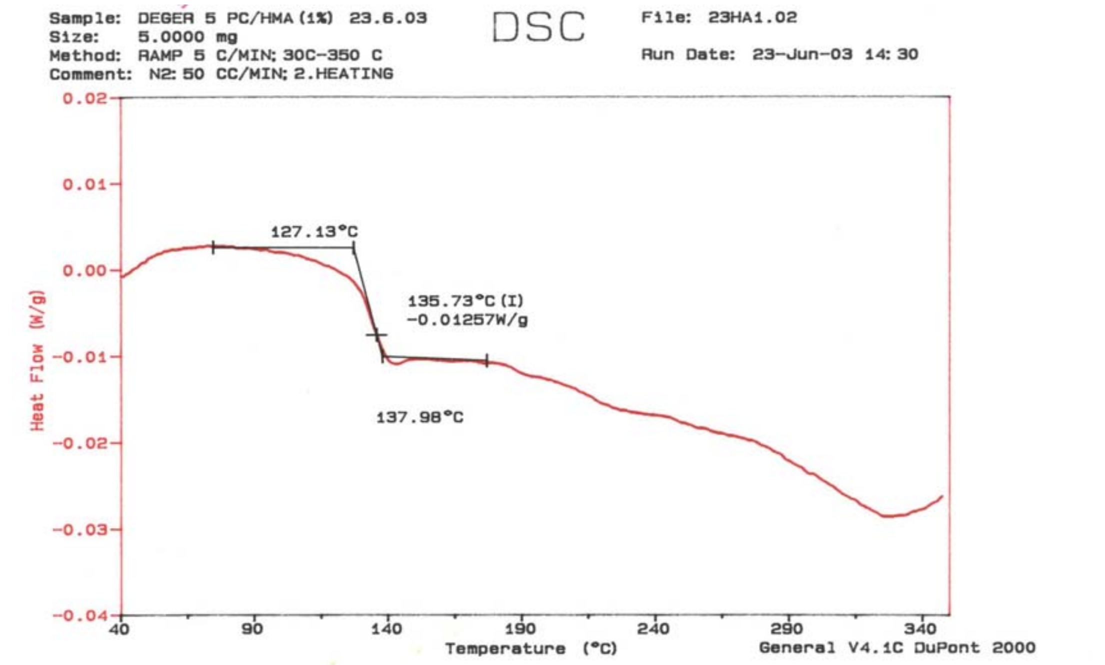


Figure C.15 The DSC graph of HMA/PC (1 w/w%) membrane (Run 2)

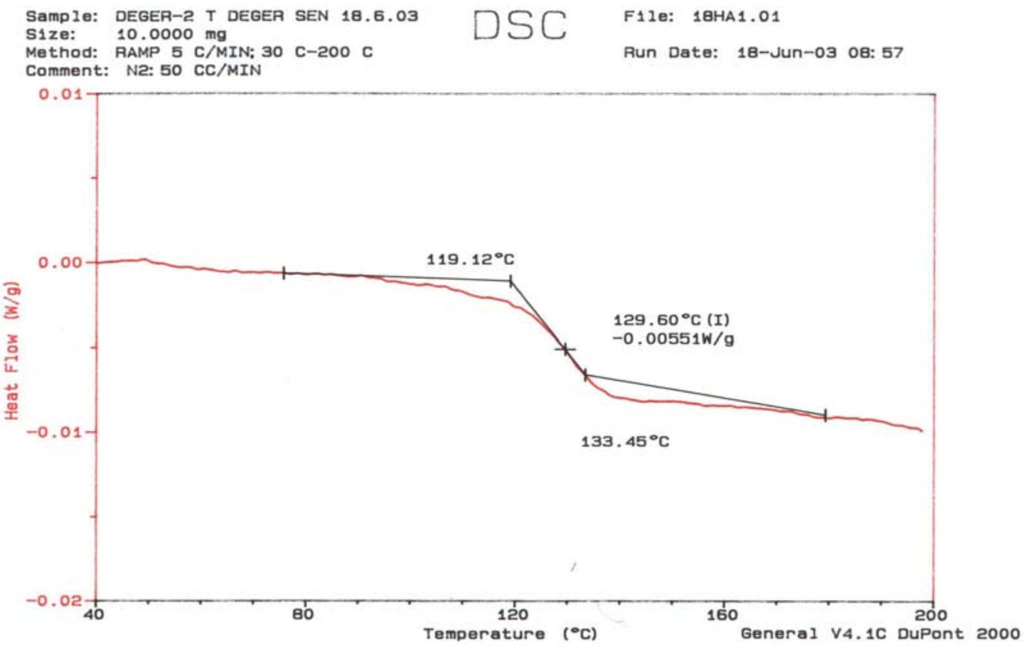


Figure C.16 The DSC graph for Catechol/PC (1 w/w%) membrane (Run 1)

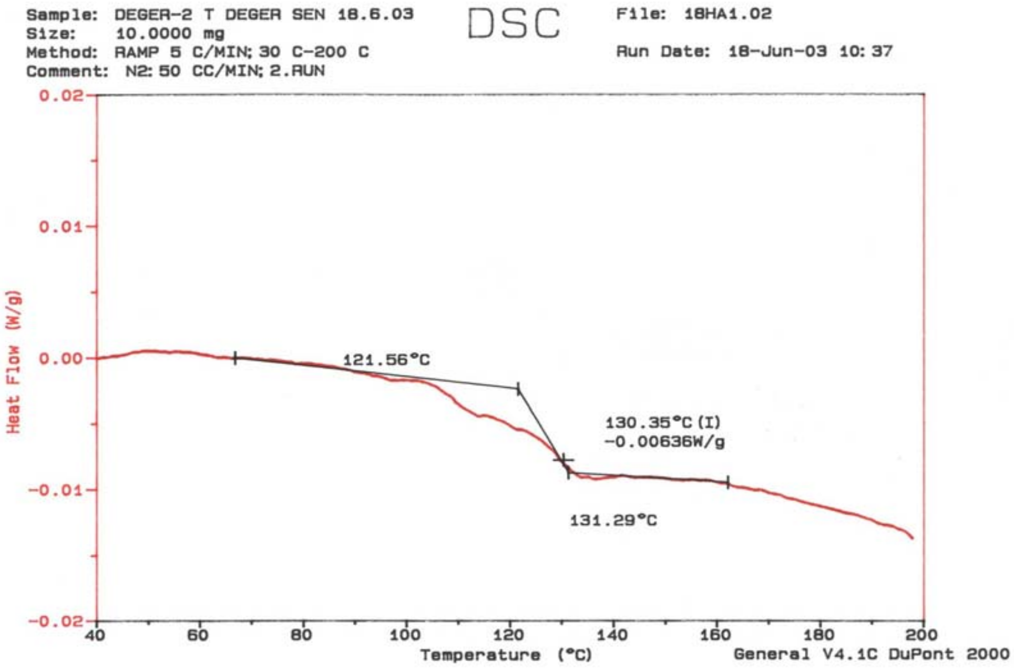


Figure C.17 The DSC graph for Catechol/PC (1 w/w%) membrane (Run 2)

APPENDIX D

DETERMINATION OF GLASS TRANSITION TEMPERATURE OF pNA WITH GORDON-TAYLOR EQUATION

Gordon-Taylor equation was applied to PC/pNA blend membrane system in order to find T_g of pNA. The equation describes the behavior of the T_g of a mixture with composition,

$$T_g = \frac{w_d T_{gd} + K w_p T_{gp}}{w_d + K w_p}$$

T_g: glass transition temperature of polymer-additive mixture (°C).

T_{gd} and T_{gp}: glass transition temperatures of the additive and polymer, respectively (°C).

w_d and w_p: weight fractions of the additive and polymer, respectively

K: adjustable parameter

In order to determine T_g of pNA the following procedure was applied:

1. Equation was rearranged such that the slope of the line gave K and the intercept gave T_{gd} ,

$$T_g = T_{gd} + K \frac{w_p}{w_d} (T_{gp} - T_g)$$

2. T_g versus $(w_p/w_d)(T_{gp}-T_g)$ plot was drawn (Figure D.1) by using four experimentally determined T_gs of PC/pNA membranes at different concentrations of pNA. T_{gp} was constant and 146 °C.

w_d	T_g	$(w_p/w_d)(T_{gp}-T_g)$
0.005	142	796
0.01	138	792
0.02	131	735
0.05	111	665

3. The least square line $y= 0.2209x - 34.5$ was drawn through the points. In this line equation slope was K and intercept was T_{gd} .

$K= 0.2209$

$T_{gd}= -34.5$ °C

4. T_g of PC/pNA membrane at 10 w% pNA concentration was determined by using Gordon-Taylor equation.

$$T_g = \frac{(0.10)(-34.5) + (0.2209)(0.90)(146)}{(0.10) + (0.2209)(146)} = 85.6 \text{ °C}$$

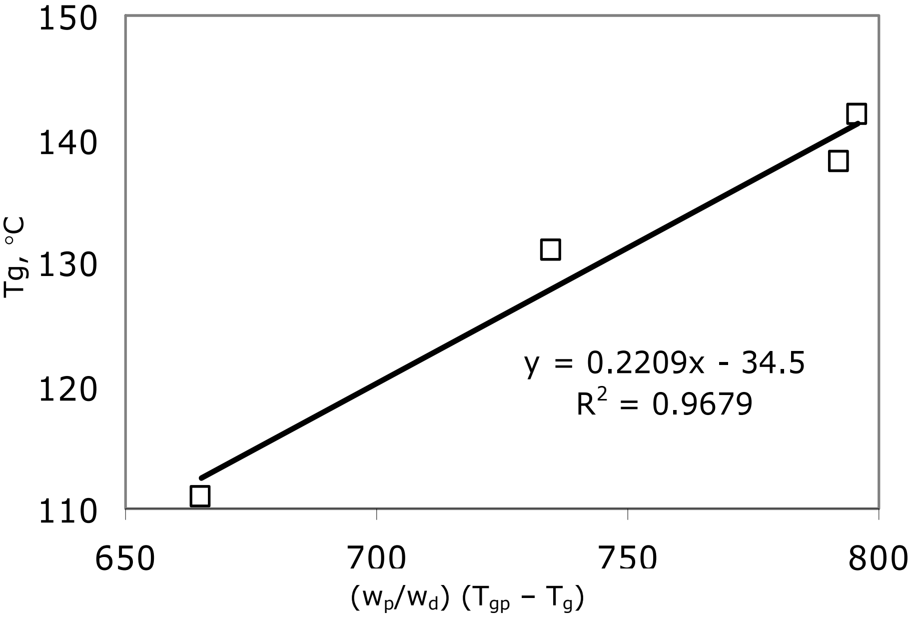


Figure D.1 T_g versus (w_p/w_d) $(T_{gp} - T_g)$ graph of PC/pNA system

APPENDIX E

FOURIER TRANSFORM INFRARED SPECTRA

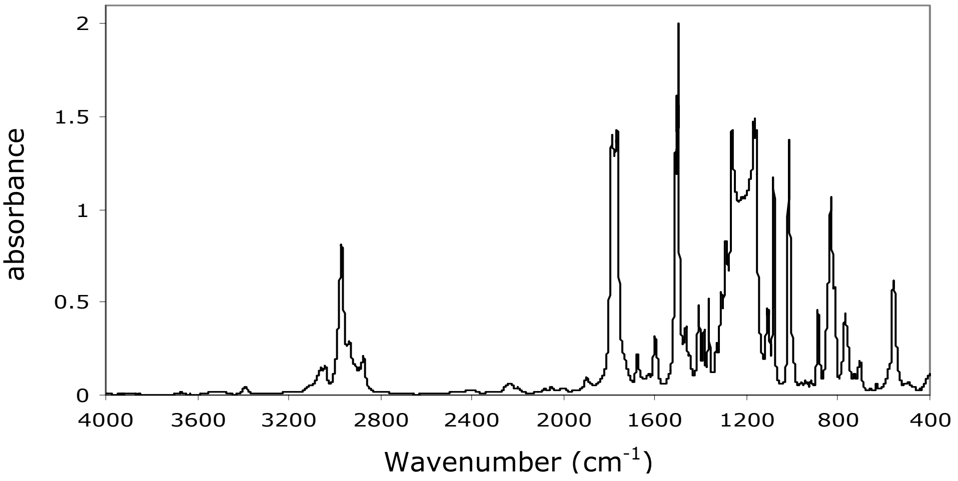


Figure E.1 FTIR spectrum of pNA/PC (0.5 w/w%) membrane

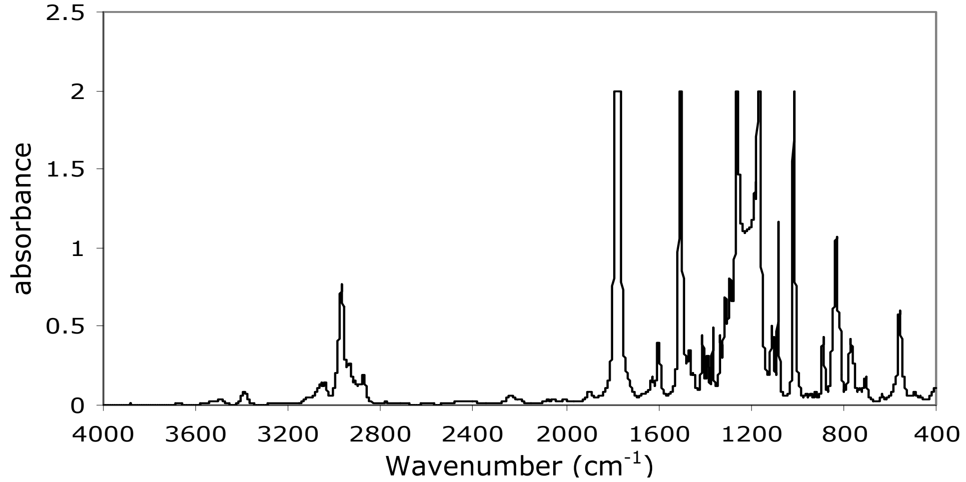


Figure E.2 FTIR spectrum of pNA/PC (2 w/w%) membrane

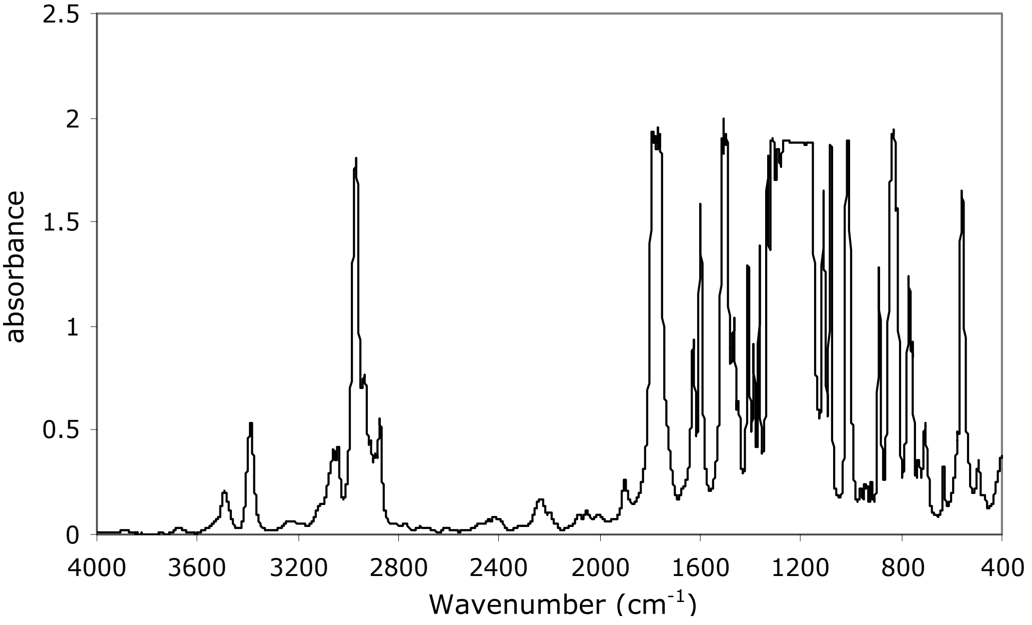


Figure E.3 The FTIR spectrum of pNA/PC (5 w/w%) membrane

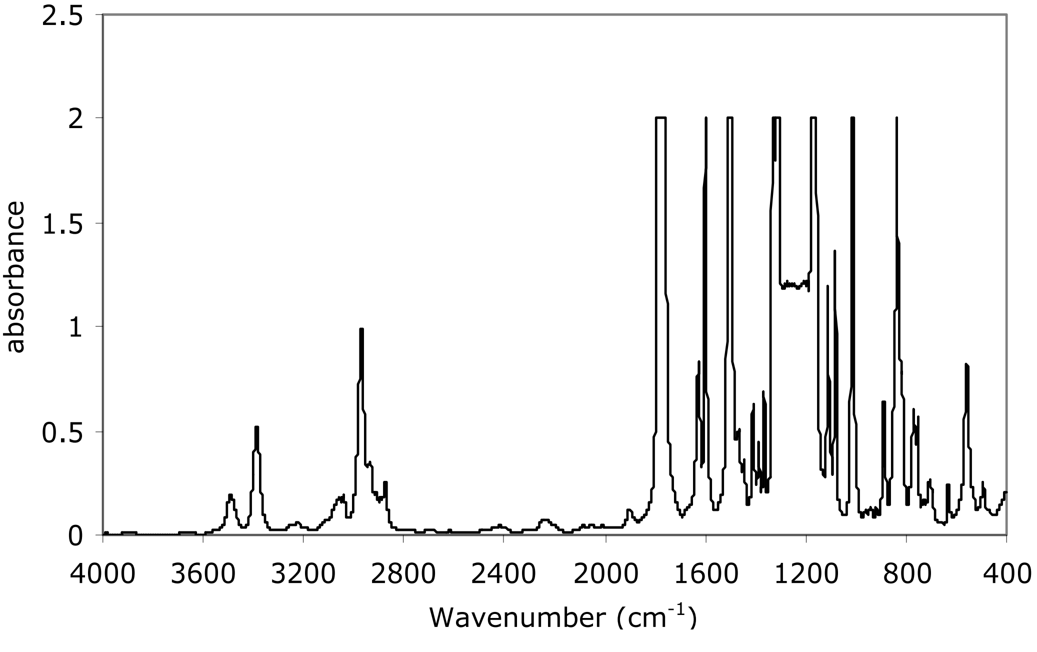
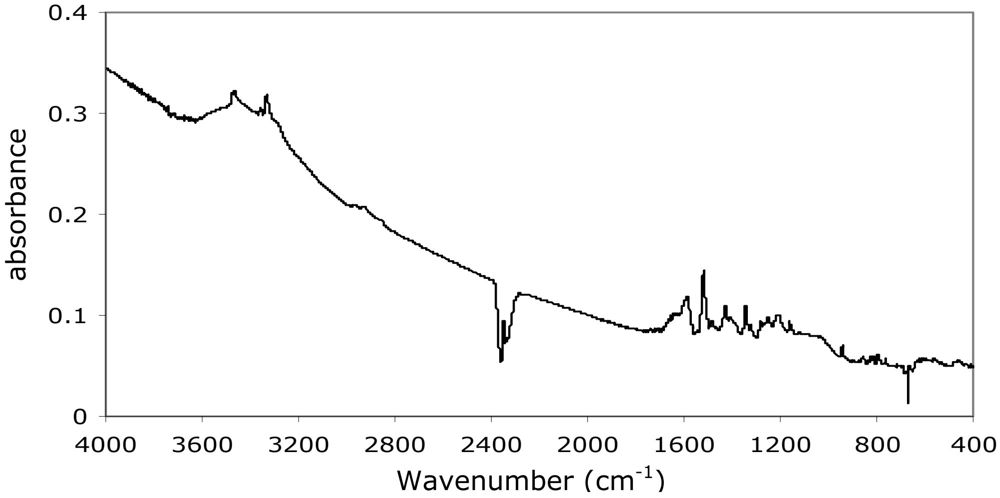


Figure E.4 FTIR spectrum of pNA/PC (10 w/w%) membrane



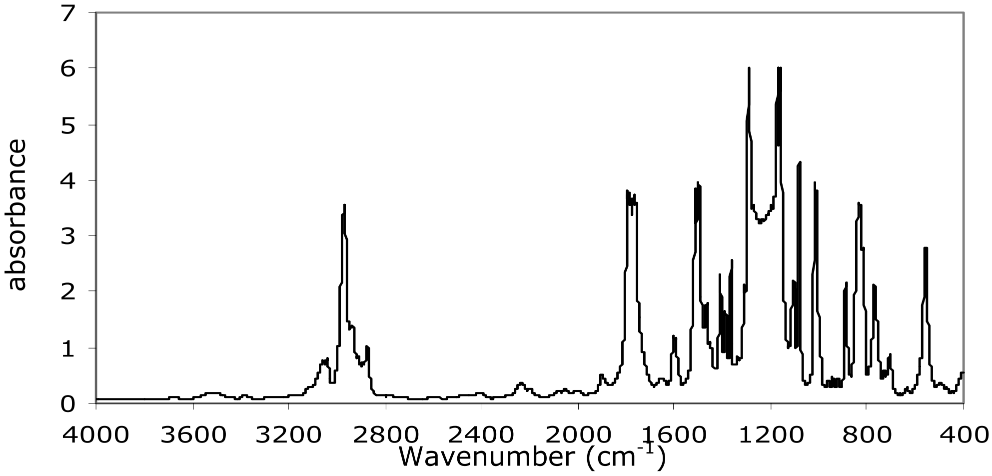


Figure E.6 FTIR spectrum of ANP/PC (1 w/w%) membrane

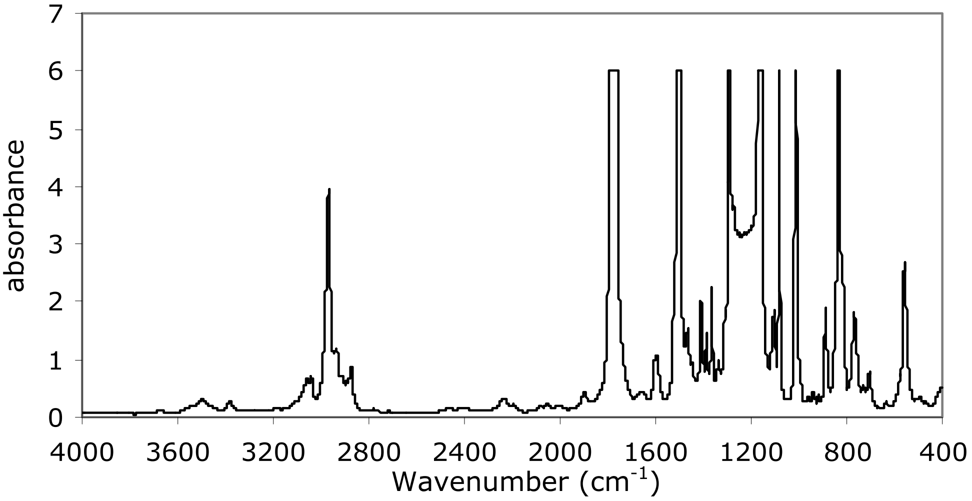


Figure E.7 FTIR spectrum of ANP/PC (2 w/w%) membrane

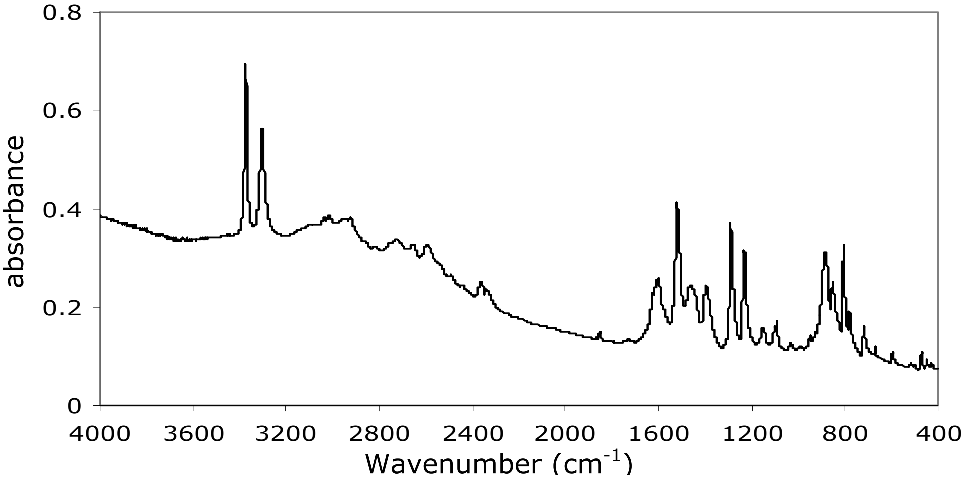


Figure E.8 FTIR spectrum of pure HMA powder (KBr pellet)

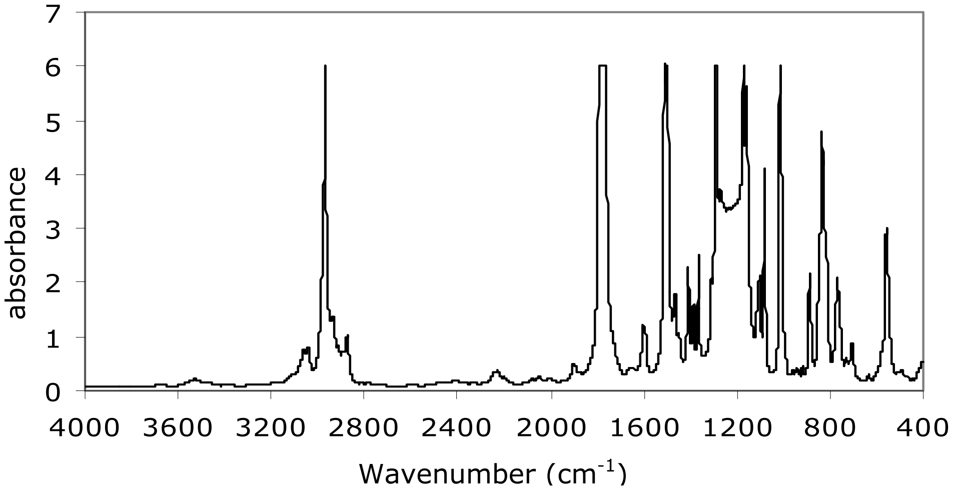


Figure E.9 FTIR spectrum of HMA/PC (1 w/w%) membrane

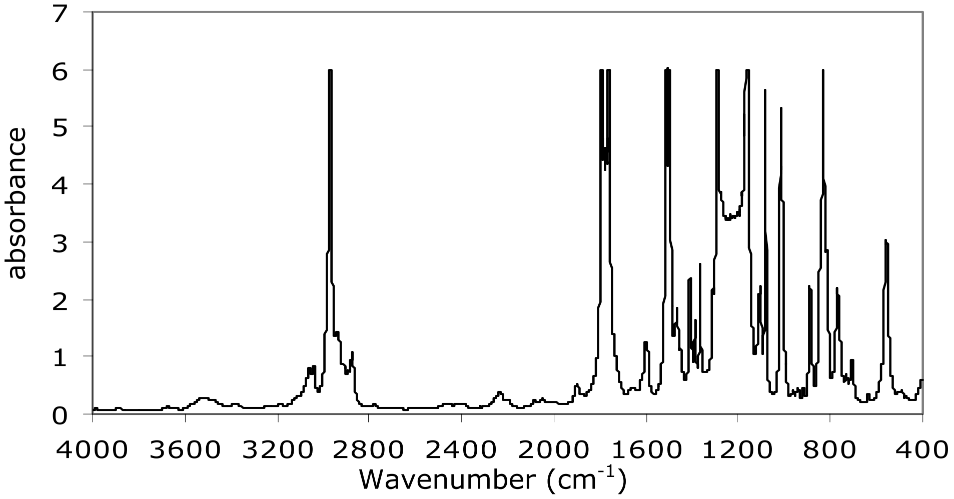


Figure E.10 FTIR spectrum of HMA/PC (2 w/w%) membrane

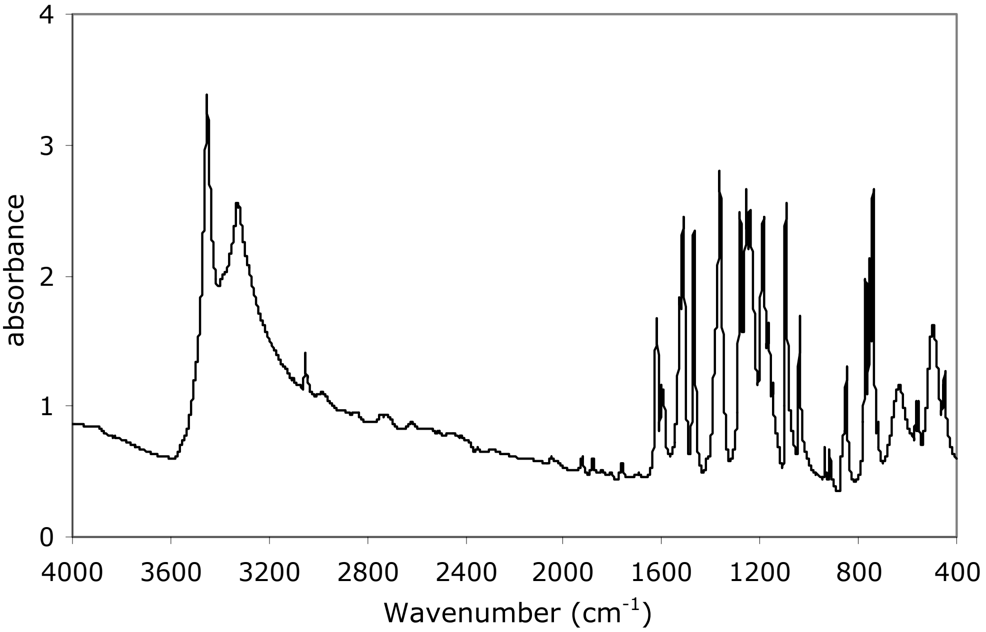


Figure E.11 FTIR spectrum of pure Catechol powder (KBr pellet)

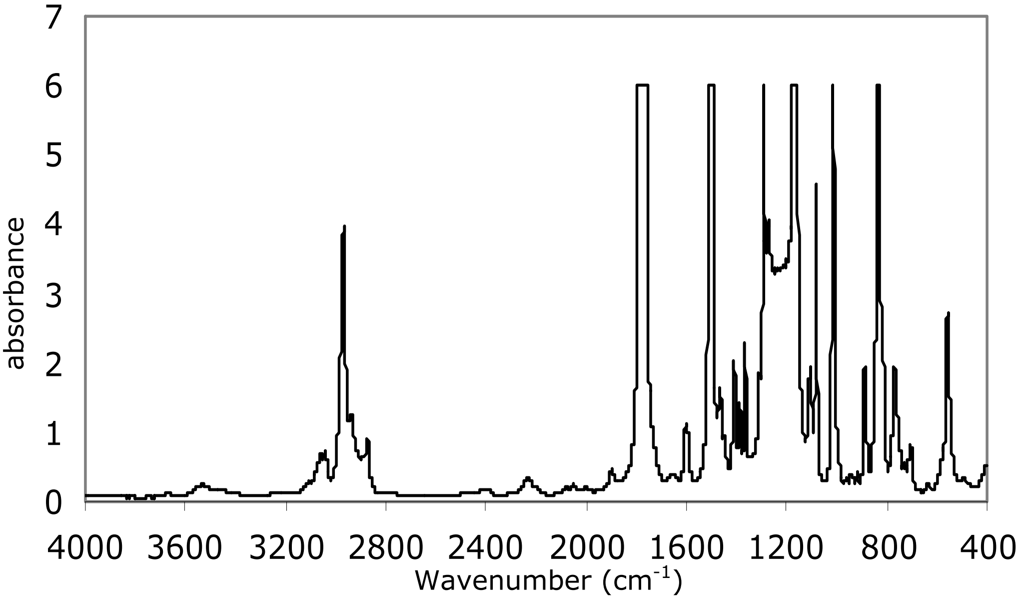


Figure E.12 FTIR spectrum Catechol/PC (1 w/w%) membrane

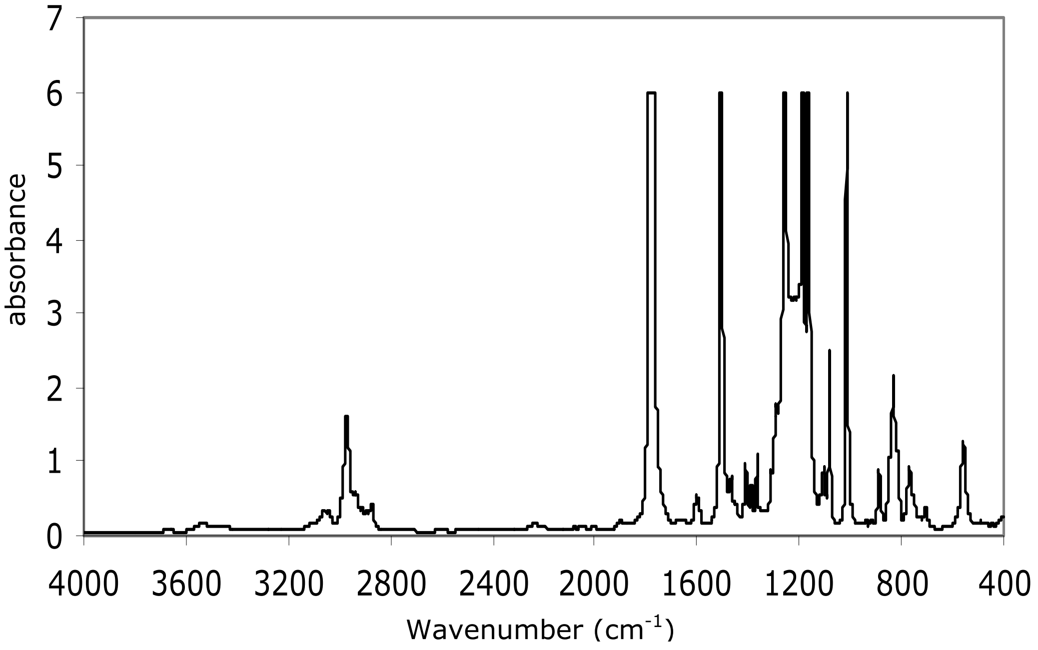


Figure E.13 FTIR spectrum Catechol/PC (2 w/w%) membrane

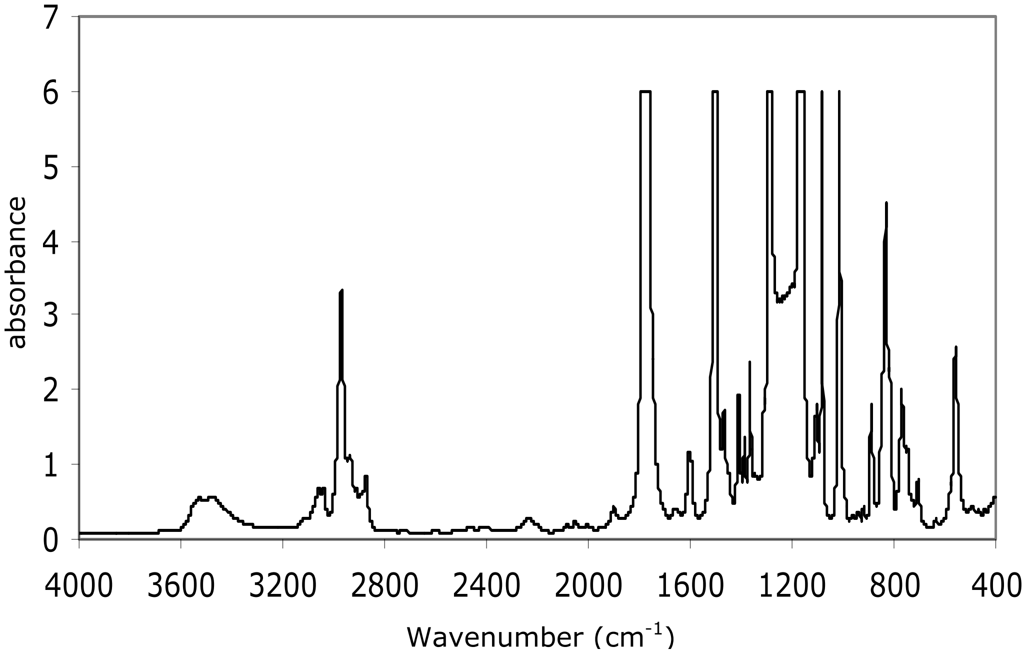


Figure E.14 FTIR spectrum Catechol/PC (5 w/w%) membrane