

## Fabrication and Characterization of Polymer Blend Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation

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### Abstract

In the last two decades, various modifying techniques have been employed to improve membranes performance including mixed matrix, cross linking, grafting, polymer blending, making composite or hybrid membrane. Blending of polymeric membrane is a cost and time effective approach and an advanced technique for gas separation, where two or more polymers are mixed to produce a new material with different and desired physical, chemical and mechanical properties. This work reports on the separation performance of a novel polymeric blend membrane based on poly(amide-b-ethylene oxide) and polyethersulfone blends. These flat sheet membranes were synthesized using solution-casting in different ratios (10-40%) in order to improve membrane separation performance of CO<sub>2</sub>/CH<sub>4</sub> gas mixtures. Prepared membranes were then characterized by Fourier Transformed Infra-Red Spectroscopy (FTIR) where spectral changes indicated existence of molecular interaction among the polymeric blends, highlighting their compatible nature. Permeabilities of pure gases (CO<sub>2</sub> and CH<sub>4</sub>) were also examined at room temperature. Results indicated that increasing wt.% PES in the Pebax®/PES blend membranes increased selectivity of CO<sub>2</sub>/CH<sub>4</sub> and decreased pure gas permeabilities.

**Keywords:** Blending, gas separation, poly(amide-b-ethylene oxide), polyethersulfone

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## Introduction

Gas separation membrane is a semi-permeable barrier, separating one or more gases from a multicomponent gas mixture by permitting the transport of certain molecules under the influence of some forms of chemical potentials such as pressure or concentration gradient (Mulder, 1997; Baker, 2000).

There are many known industrial processes involving separation of carbon dioxide from other gases including purification of synthesis gas to obtain high purity hydrogen for fuel cells, removal of carbon dioxide in natural gas sweetening, separation of carbon dioxide from industrial flue gases for greenhouse gas sequestration and removal of carbon dioxide from breathing air in space crafts or spacesuits (Dortmundt and Doshi, 1999; Chung et al., 2007). Table 1 summarizes several sweetening technologies commercialized to date for such purposes (Maddox and Morgan, 1998).

Among these techniques, membrane separation has attracted much attention due to its compact and modular devices, mild operating

conditions, simple equipment without moving parts (Ismail and Kusworo, 2007; Shekhawat et al., 2003), while it could be scaled up easily for design purposes (Shekhawat et al., 2003) and does not require sorbent regeneration or desorption (An et al., 2011).

A desirable membrane should satisfy several structural and functional properties including a combination of high permeation rate, high species selectivity, low fouling rate, long and reliable service life, and adequate mechanical, thermal and chemical stabilities under certain operating conditions (Meinema et al., 2005). However, a single membrane cannot surpass all above requirements and hence, attempts are continually being made to compensate for these using polymeric blend membranes which offer extensive processability.

As far as the ratio of glass transition and application temperatures are concerned, there are two types of polymeric membranes: glassy and rubbery. The former have a glass transition temperature higher than application temperature, while the latter refers to those polymeric membranes having glass transition temperatures well below their application

Table 1- Classification of sweetening Technology

CO <sub>2</sub> Removal Mechanism	Process Type	Technology	Commercial Name
Chemical absorption	Regenerative, continuous	Potassium carbonate	MEA, DEA, MDEA, DIPA, DGA, formulated solvents
	Non regenerative, continuous (usual arrangement : lead/lag)	Sodium hydroxide	Benifielf, Catacarb, Giam macro-Vetrocoke, etc.
Physical absorption	Regenerative, continuous	Physical solvents	-
Physical-chemical absorption	Regenerative, continuous	Physical-chemical solvents	Selexol, Rectisol, Purisol, Fluor Solvent, IFPexol, etc.
Physical adsorption	Regenerative, continuous (adsorption/desorption sequence)	Molecular sieves	Z5A (Zeochem), LNG-3 (UOP), etc.
Permeation	Continuous	Membranes	Separex, Cynara, Z-top, Medal, etc.

temperatures (Mulder, 1997). A limiting challenge in the industrial application of polymeric membrane is their low permeability and selectivity, for which blending with other polymers are thought to be the right approach in meeting this challenge.

poly(amide-b-ethylene oxide) (Pebax®1657) seems to be a suitable choice for this as it is a rubbery copolymer containing PEO segments as the permeable phase, with the polyamide crystalline phase giving the required mechanical strength to the membrane. It also has a high CO<sub>2</sub> permeability due to the high affinity of its PEO segment with respect to the polar CO<sub>2</sub> molecule, making it a promising material for CO<sub>2</sub> capturing of flue gas and in natural gas sweetening processes (Car et al., 2008; Okamoto et al., 1995; Bondar et al., 2000). Polyethersulfone (PES) on the other hand, offers high chemical resistance, and is stable against oxygen and thermal degradation with high CO<sub>2</sub>/CH<sub>4</sub> selectivity while being commercially attractive (Çakal, 2009). Therefore, adding PES to Pebax® may improve the CO<sub>2</sub>/CH<sub>4</sub> selectivity of this rubbery polymer, and hence in this study, we first prepared the Pebax®/PES blend membranes with different ratios and characterized them before gas transport properties of the blend membranes were investigated and compared with those of the neat Pebax®. To the best of our knowledge, apart from our own research papers currently under review, blending of these rubbery/glassy polymers has not been reported elsewhere in the literature.

## Experimental

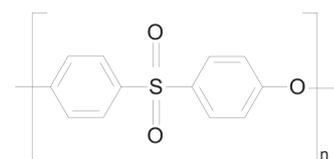
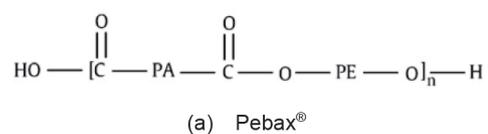
### Material

Pebax® 1657 was purchased from Arkema and PES was supplied from BASF, with their chemical structure being presented in Fig. 1. Dimethylacetamide (DMAc) was purchased from Merck and used as solvent in its received form.

### Preparation of films

Polymeric blend membranes with various

compositions (10/90, 20/80, 30/70, 40/60 wt.%) were prepared by solution-casting and evaporation method. First, PES in stipulated quantity was dissolved in DMAc using a magnetic stirrer for 12 h. Subsequently, Pebax® was added while stirring was continued at 90 °C to allow complete mixing of the polymers. The solution was cast into a 10 cm diameter Petri-dish, and kept in an oven at 60 °C for 16 h. All membranes were kept under vacuum at room temperature overnight before testing was conducted on them.



(b) PES

Fig. 1- Chemical structures of (a) Pebax® and (b) PES

### Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Alpha FTIR to examine the chemical interaction between the polymers. Measurements were carried out using the attenuated total reflectance (ATR) technique.

### Gas permeability

Pure gas permeation properties were determined using constant pressure/variable volume method for both CO<sub>2</sub> and CH<sub>4</sub>. All measurements were performed at room temperature and volume change under constant feed pressure was measured by means of a capillary tube.

Permeability, an intrinsic property of the membrane material, is defined according to the following equation:

$$(1) P_i = \frac{LN_i}{\Delta P_i}$$

where  $P_i$  represents the permeability for penetrant component  $i$ ,  $L$  is the membrane thickness (cm) and  $N_i$  refers to the flux passing through the film ( $\text{cm}^3/\text{sec}$ ). Its unit is commonly expressed in Barrer ( $1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm}/(\text{cm}^2 \text{ sec cmHg})$ ). The ability of a membrane in separating two molecules, for example,  $i$  and  $j$ , is referred to as the ratio of their permeabilities, or better known as the membrane selectivity. In this study, ideal gas selectivity was calculated from the ratio of pure gas permeability according to equation (2) below (Mulder, 1997):

$$(2) \alpha_{i,j} = \frac{P_i}{P_j}$$

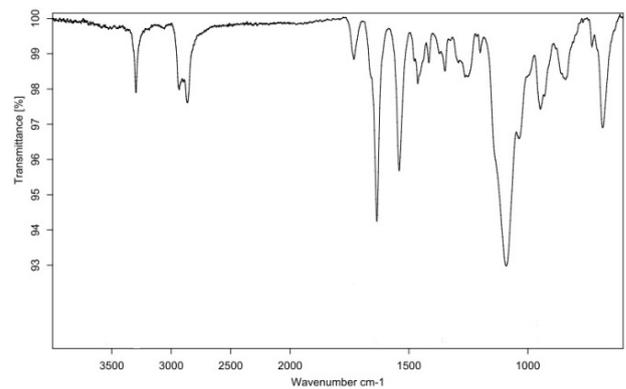
## Results and discussion

### FTIR Analysis

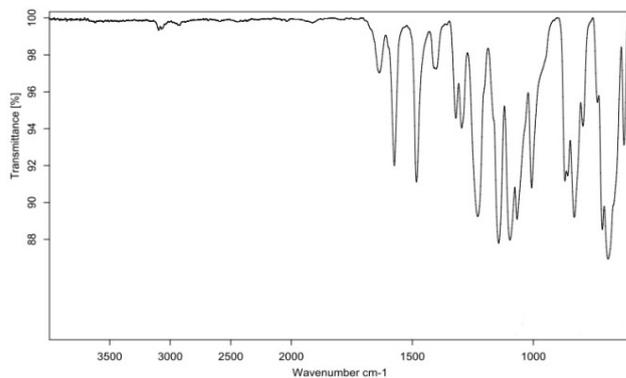
Fig. 2 demonstrates FTIR-ATR spectra of Pebax®, PES and Pebax®/PES (20 wt.%) blend membranes. As can be seen,  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  stretching vibrations in Pebax® were located at  $1731$  and  $1090 \text{ cm}^{-1}$ , respectively. Moreover, bands at  $1635$  and  $3296 \text{ cm}^{-1}$  could be attributed to presence of both  $\text{C}=\text{O}$  and  $\text{N}-\text{H}$  of the amide functional group, respectively (Kim and Lee, 2001), while the band at  $1540$  may be related to  $\text{N}-\text{H}$  bending. In the PES spectrum, the  $\text{S}=\text{O}$  stretching peaks were situated at  $1143 \text{ cm}^{-1}$  and  $1007 \text{ cm}^{-1}$ , while the  $\text{C}-\text{H}$  stretching peak of benzene ring was located at  $3096 \text{ cm}^{-1}$ . Other bands at  $1574$ ,  $1482$  and  $1402 \text{ cm}^{-1}$  might be assigned to aromatic skeletal vibrations. The characteristic peaks at  $1320 \text{ cm}^{-1}$  and  $1230 \text{ cm}^{-1}$  may also be attributed to  $\text{C}-\text{O}-\text{C}$  stretching (Qu et al., 2010).

As for the Pebax®/PES (20 wt.%) blend membrane, apart from Pebax® characteristic peaks which were clearly evident, the  $\text{N}-\text{H}$  peak was found to be gradually split into two peaks;

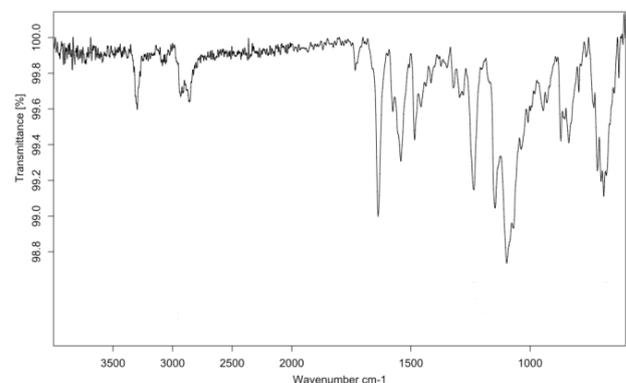
the free  $\text{N}-\text{H}$  in the Pebax® structure as well as a hydrogen bonded one with  $\text{S}=\text{O}$  group appeared at  $1542 \text{ cm}^{-1}$ . In other words, an intermolecular hydrogen bond may have been formed between the amidic hydrogen and the sulfone group. This weak intermolecular interaction, has led to longer  $\text{N}-\text{H}$  bond and hence wavelength vibration of the bonded  $\text{N}-\text{H}$  has become higher than the free one. This could be treated as evidence for PES being kept in the Pebax® matrix.



(a)



(b)



(c)

Fig. 2- FTIR-ATR of (a) pure Pebax® (b) pure PES (c) Pebax®/PES (20 wt.%)

## Permeability results

Figs. 3 and 4 illustrate pure gas permeabilities and ideal selectivities of both neat and blend membranes using CO<sub>2</sub> and CH<sub>4</sub>, respectively. In general, CO<sub>2</sub> permeability is higher than CH<sub>4</sub>, and CO<sub>2</sub> has greater solubility in Pebax® polymer. The kinetic diameter of CO<sub>2</sub> (3.3 Å) (Bakhtiari et al., 2011; Li et al., 2013) is also smaller than that of CH<sub>4</sub> (3.8 Å) (Li et al., 2013; Karkhanechi et al., 2012), which leads to its greater diffusivity.

Compared to pure Pebax® membrane, blend

membranes exhibit improved CO<sub>2</sub> selectivity perhaps due to the presence of PES in the blend, while compared to pure PES membrane, these membranes exhibit improvement in the permeability due to the presence of Pebax® in the blend. Adding PES as glassy polymer to Pebax® matrix has led to a decrease in the chain mobility of the Pebax®, and hence reduced permeability. Because of size sieving properties of the glassy polymers, PES presence in Pebax® has apparently increased selectivity here.

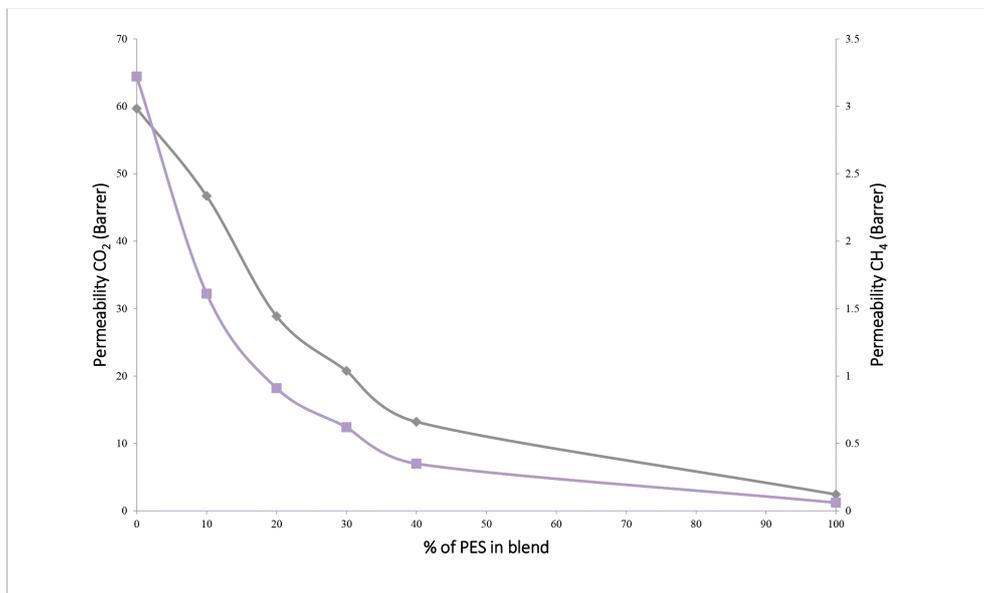


Fig. 3 – Pure gas permeabilities for Pebax®/PES blend membranes

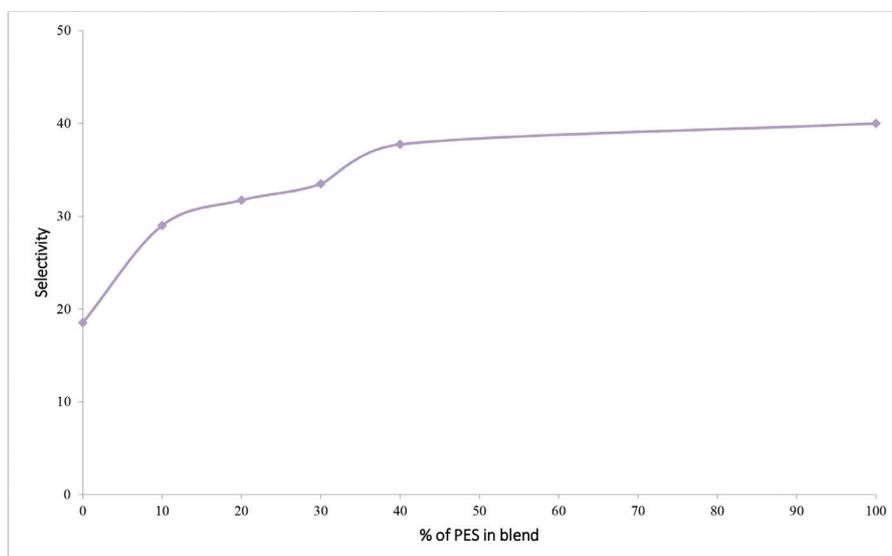


Fig. 4 – Ideal selectivities for Pebax®/PES blend membranes

## Conclusion

In fabricating a novel polymeric blend membrane to separate CO<sub>2</sub>/CH<sub>4</sub> gas mixtures, based on poly(amide-b-ethylene oxide) and polyethersulfone blends, flat sheet membranes were synthesized using solution-casting in different ratios (10-40%), where all prepared membranes were of clear and homogeneous films. FTIR analysis confirmed presence of PES in Pebax® matrix. Spectral changes indicated existence of molecular interaction among the polymeric blends, highlighting their compatible nature. Increasing wt.% PES in the Pebax®/PES blend membranes, increased selectivity of CO<sub>2</sub>/CH<sub>4</sub> while decreasing pure gas permeabilities. Gas permeabilities of flat sheet blend membranes varied monotonically between those of the two pure polymers. For further work we intend to add fillers in the blend, in order to enhance even further the polymeric blend membrane performance.

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## ساخت و ارزیابی غشاهای آمیزه پلیمری برای جداسازی CO<sub>2</sub>/CH<sub>4</sub>

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### چکیده

در دو دهه گذشته، تکنیک‌های اصلاحی مختلف برای بهبود عملکرد غشا شامل غشاهای ماتریس آمیخته، ایجاد اتصال عرضی، پیوندسازی، آمیزه‌سازی پلیمری، ساخت غشاهای کامپوزیتی یا ترکیبی بکارگرفته شده است. استفاده از آمیزه‌سازی غشاهای پلیمری، رویکردی کم هزینه و سریع و در عین حال، تکنیکی پیشرفته برای جداسازی گاز است که در آن، دو یا چند پلیمر برای تولید ماده‌ای جدید با خواص متفاوت فیزیکی، شیمیایی و مکانیکی بکاربرده می‌شوند. در این مقاله، عملکرد جداسازی غشا آمیزه پلیمری جدیدی، بر پایه پلی (آمید-B اکسید اتیلن) و پلی اترسولفون گزارش می‌شود. این غشاهای تخت با استفاده از روش قالب‌گیری محلول در نسبت‌های مختلف (10-40%) به منظور بهبود عملکرد جداسازی غشایی مخلوط گازهای CO<sub>2</sub>/CH<sub>4</sub> تهیه شدند. ویژه‌گی‌های غشاهای ساخته شده سپس توسط آنالیز طیف‌سنجی تبدیل فوریه مادون قرمز (FTIR) ارزیابی شدند، بطوری که تغییرات طیفی در آن حاکی از تعامل متقابل مولکولی داشت و سازگاری طبیعت میان پلیمرها در این آمیزه را تایید می‌کرد. نفوذپذیری گازهای خالص (CO<sub>2</sub> و CH<sub>4</sub>) نیز در دمای اتاق مورد بررسی قرار گرفت. نتایج نشان داد که افزایش درصد وزنی PES در غشا آمیزه Pebax®/PES سبب افزایش گزینشگری CO<sub>2</sub>/CH<sub>4</sub> و کاهش نفوذپذیری گازهای خالص گردید.

واژگان کلیدی: آمیزه‌سازی، جداسازی گازی، پلی (آمید-b-اتیلن اکساید)، پلی اترسولفون