Synthesis and characterization of polymeric blend membranes enhanced by monoethanolamine for CO₂/CH₄ separation

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Gas separation membranes for natural gas are widely used. For efficient separation of CO₂/CH₄, high-performance gas separating polymeric blend membranes are desired. The main objective of this study is to synthesize blend membranes for removal of CO₂ from CH₄ using glassy and rubbery polymers with the addition of amine. The methodology comprises various contents of polyvinyl acetate (PVAc) ranging from 5 to 20 wt% blended with polysulfone (PSU) and 10 wt% MEA in DMAc solvent used for the formation of flat sheet membranes *via* solution casting method. The synthesized blend membranes possessed homogenous surfaces and showed a uniform packed bed of spherical structure, as seen from FESEM images. The existence of a single glass transition temperature for different blend membranes indicated miscibility among the polymeric blends, shown by DSC analysis. Thermogravimetric analysis showed an improvement in the maximum degradation temperature with the increase in PVAc content in the membrane blends. FTIR analysis confirmed the polymer blend's miscibility with very few spectral peak shifts. The gas permeation results concerning MEA showed that CO₂ permeance increased, in PSU and PSU 80%/PVAc 20%, from 39.63% to 63.97% at 2 bar pressure. EPBM is an appropriate tool for the production of novel materials with joined characteristics that improved application properties with low-cost advantage.

Keywords: Polymeric blend membranes; Monoethanolamine; Morphology; Thermal degradation temperature; Spectral analysis.

INTRODUCTION

The performance of gas separating membranes is quite important for effective separation of CO₂ from natural gas. For membrane synthesis, permeance and selectivity are essential parameters that need to be addressed for efficient CO₂ separation [1, 2]. In gas separation, many glassy polymers have been used for membrane fabrication based upon industrial or scientific research work. Polysulfone was considered because of its good thermal, mechanical and chemical stability along with satisfactory gas performance [3, 4]. The same characteristics of polyvinyl acetate (PVAc) along with its comparatively low price, piezoelectric, pyroelectric and ferroelectric properties [5, 6] define its main advantages as flexibility, low density and formability [7]. Table 1 shows the different studies on polymer blended membranes [8-20].

Different modifications were employed to improve membrane performance. Monoethanolamine (MEA), which belongs to primary amines, is widely used for removing CO_2 from natural gas; it is a relatively strong base having high reactivity with CO_2 , low cost of solvent, thermal stability, but it was replaced by more efficient systems because of its corrosive properties, degradation of solvent issues, high heat of reaction with CO_2 and considerable energy requirements for regeneration of solvent used [21].

Numerous researchers have considered the chemistry of CO_2 -amine solutions over many years due to its significant industrial application for CO_2 removal from gas streams. The Danckwerts' zwitterions mechanism has become the most frequently accepted mechanism for CO_2 -amine reaction [22]. The reactions between CO_2 and primary amines are shown below, R representing the functional group for MEA:

$$R_1 = -H, R_2 = -CH_2CH_2OH$$

 $R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+COO^-$ (Zwitter ion) (1)

$$R_1 R_2 NH^+ COO^- + R_1 R_2 NH \leftrightarrow$$

$$R_1 R_2 NCOO^- (Carbamate)$$
(2)

Overall reaction is:

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH^+ \quad (3)$$



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The amine solution has shown efficient capability for natural gas purification in an absorption process [22]. Hence, it is expected that by blending with glassy polymer using different alkanolamine solutions, the separation ability of a blended polymeric membrane for the CO₂/CH₄ mixture will be enhanced. Different alkanolamines have different reaction rates with various acid gases. Furthermore, these alkanolamines differ in their equilibrium absorption characteristics for the many acid gases and have different sensitivities to corrosion factors and solvent stability. In MEA (primary amine), the CO_2 is captured by a chemical absorption process, in which the carbon dioxide reacts with the primary amine in the form of a carbamate. The main objective of this study is to synthesize an enhanced polymeric membrane with the addition of amine.

Year	Polymers	Gas type	Remarks	Permeance	Selectivity
2006	PU based PEI/PAI (Glassy/Glassy) blend	CO ₂ /N ₂	CO ₂ /N ₂ selectivity of PU- based blend membranes was increased	P _{CO2} =20.06 Barrer	$\alpha \frac{CO_2}{N_2} = 22.56$
2006	PU/PDMS (Rubbery/Rubbery) cross-linked	CO ₂ /CH ₄	Highest permeability, diffusivity, and solubility values are found for the PDMS membranes.	P _{CO2} =10 Barrer	$\alpha \frac{CO_2}{CH_4} = 0.41$
2008	PES/PI (Glassy/Glassy) blend MMM	O_2/N_2	Ideal separation factors of O ₂ /N ₂ is increased	P _{O2} =4.2 Barrer	$\alpha \frac{O_2}{N_2} = 3.8$
2009	PVAm/PVA with porous PES support	CO ₂ /N ₂	Ultra-thin membrane with good strength, stability and permeability/ selectivity	P _{CO2} =0.58 m ³ (STP) /(m ² h bar)	$\alpha \frac{CO_2}{N_2} = 74$
2010	PEG/PDMS	CO ₂ /CH ₄	Remarkably, the CO ₂ /H ₂ selectivity is enhanced	P _{CO2} =530 Barrer	$\alpha \frac{CO_2}{CH_4} = 10$
2010	PES/PI (Glassy/Glassy)	O ₂ /N ₂	Gas permeance of N ₂ increased with increase in feed pressure	P ₀₂ =210.8 GPU	$\alpha \frac{O_2}{N_2} = 5.4$
2011	SPEEK/ Matrimid	CO ₂ /CH ₄	Cross-linked for anti- plasticization	P _{CO2} =9.43 Barrer	$\alpha \frac{CO_2}{CH_4} = 27.98$
2011	PEI/PVP	CO ₂ /CH ₄ , CO ₂ /N ₂	Significant improvement in selectivity	P _{CO2} =1.66 GPU	$\alpha \frac{CO_2}{CH_4} = 55.33$
2012	PIM-1/ Matrimid	CO ₂ /CH ₄ , CO ₂ /N ₂	Increased selectivity	P _{CO2} =50 Barrer	$\alpha \frac{CO_2}{CH_4} = 31$
2013	PSF/PVP	CO ₂ /CH ₄	Studied effect of solvents	P _{CO2} =275 GPU	$\alpha \frac{CO_2}{CH_4} = 5.75$
2013	PU/PVA	CO ₂ /CH ₄	Increased CO ₂ permeability	P _{CO2} =49.5 Barrer	$\alpha \frac{CO_2}{CH_4} = 10.1$
2013	PEG-PDMS	CO ₂ /N ₂	Significant improvement in selectivity	P _{CO2} =20.0 GPU	$\alpha \frac{CO_2}{N_2} = 18$
2014	CA/TiO ₂ blend	CO ₂ /CH ₄	Permeability of CO ₂ was found to be increased for CA–TiO ₂ blended	$P_{CO2}=3.43x$ 10^3 Barrer	$\alpha \frac{CO_2}{CH_4} = 23.3$
2015	PES/PVAc	CO ₂ /CH ₄	CO ₂ permeance increase due to the addition of PVAc in PES	P _{CO2} =4.15 GPU	$\alpha \frac{CO_2}{CH_4} = 1.40$
2016	PSF/PI	CO ₂ /CH ₄	Improved selectivity	P _{CO2} =3.3 Barrer	$\alpha(\frac{CO_2}{CH_4}) = 13.06$

Table 1. Different	studies o	on blend	membranes
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	Polyı	Amine, 10 wt.%		
Membrane	PSU, wt. % PVAc, wt. %			
M1	100%	0%		
M2	0%	100%	-	
M3	95%	5%		
M4	90%	10%		
M5	85%	15%	MEA	
M6	80%	20%		

A. *Mushtaq et al.*: *Synthesis and characterization of polymeric blend membranes enhanced by.* **Table 2.** Blend composition of different polymer blend membranes

METHODOLOGY

Materials

Polysulfone (PSU Udel® P-1800 powdered grade with a glass transition temperature (T_g) of 185°C) was purchased from Solvay Advanced Polymers, L.L.C, U.S.A. Polyvinyl acetate (PVAc beads, average Mw ~100,000 by GPC with a glass transition temperature (T_g) of 28°C) was supplied by Sigma-Aldrich, Germany. Dimethylacetamide (DMAc 99.99% pure) was acquired from Merck, Germany. MEA amine 99.99% pure was purchased from Merck, Germany. Amines were used for the fabrication of polymeric amine blend membranes.

Method

Two different types of membranes were prepared in this work: polymeric blend membranes and polymeric amine blend membranes. To prepare the membranes, the following procedure is given:

i. PSU was heated at 110° C to remove moisture content. Then, the PSU and PVAc were allowed to dissolve completely in DMAc solvent.

ii. Then the amine was added in the blend with continuous stirring for 24 h to obtain a homogeneous dope solution.

iii. To remove air bubbles, the solution was ultrasonicated in Transonic Digital S, Elma® for 3 h at a frequency of 100 Hz.

iv. This blend was poured and cast on a glass plate using a casting knife with an opening of 200 μ m. After 1 h of evaporation, the casted film was dried in an oven at 70°C for 2 h. These membranes were also dried at ambient temperature for five days to allow the evaporation of the solvent.

The synthesized membranes were then peeled off for further characterization. The different compositions of polymers and amines of blend membranes are shown in Table 2.

The enhanced polymeric blend membrane was developed by blending polysulfone glassy polymer and rubbery polymer polyvinyl acetate with mono ethanol amine was carried out in the solvent dimethylacetamide. Figure 1 represents the flow diagram of a methodology for fabrication of amine

polymer blend membrane. These synthesized membranes were characterized by the following methods:

The thermal degradation temperature of the synthesized polymeric blended membranes was determined by TGA (thermal gravimetric analysis). Approximately 10 mg of the sample was heated at a rate of 2°C/min with the Perkin Elmer TGA. The CO2SMU apparatus was used for the gas permeation experiment, where CO₂/CH₄ flow rate (0.1 m³/sec) was controlled by a flow meter/controller. These trials were accomplished at room temperature ($302\pm 2K$) under ambient pressure (101 ± 2 kPa).

The FTIR spectrum was taken on a Perkin Elmer Spectrum One FTIR spectrometer, to investigate the interaction between both polymers and amine. The scans were 20 in the wavelength range of 4000 cm⁻¹ -450 cm⁻¹ and the spectra were obtained from a 200µm diameter sampling area. Membrane samples were cut from casted membrane films at random positions dried for more than 48 h at room temperature and then fixed to the plate. All spectra were corrected for the FTIR characteristic progressive increase in the absorbance at lower wave numbers, using the equipment software.

RESULTS AND DISCUSSION

Morphology of enhanced polymeric blend membranes (EPBM)

MEA amine was blended with different compositions of PVAc in a PSU matrix, the morphology of blended membranes is shown in Figures 2 to 5. It is evident from the top surfaces of Figures 2 (a) to 5 (a) that their surfaces were likewise uniform without any pin holes and no indications of phase separation. Respectively, on distinct crosssections of Figures 2 (b) to 5 (b) the enhanced polymeric blend membranes are highly packed with uniform microspheres known as a packed bed of spheres. Nevertheless, the measure of the structure is A. Mushtaq et al.: Synthesis and characterization of polymeric blend membranes enhanced by... somewhat dissimilar because of 5-20 wt. % compositions of PVAc in PSU with 10 wt. % of MEA.



Fig. 2. Blend membrane of PSU/PVAc (95/5) wt. % / MEA (a) Top view (500 ×) (b) Cross section view (200 ×)

For EPBM with MEA these figures show that membranes top surfaces were uniform and without any phase separation which suggests that miscibility exists between PSU/PVAc and MEA. Similarly, on comparing the cross-sections in Figures 2 (b) to 5 (b), the EPBM contained a uniform packed bed of spheres. The sizes of the packed bed of spheres structure increase the percentage of PVAc from 5-20 wt. % with MEA, the sphere size was found from $22.40-9.73\mu m$ and extent toward $41.06-10.64\mu m$.

To decrease the interfacial area with dispersed morphology in blends, shape relaxation of the deformed particles may occur latter, tending to acquire a spherical shape [23]. When the different compositions of PVAc are blended in PSU with different amines the wall area decreases because PVAc and amines are incorporated into the spheres. From the microporous structures of the blended membranes it is apparent that the surfaces are reasonably homogeneous indicating miscibility between the PSU/PVAc polymers and amines [24]. In addition, the number of spheres differs depending on PVAc composition and addition of MEA amine. This is probably because thermodynamic instability overcomes the kinetic process [24].

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Fig. 3. Blend membrane of PSU/PVAc (90/10) wt. % / MEA (a) Top view (500 ×) (b) Cross section view (200 ×)



Fig. 4. Blend membrane of PSU/PVAc (85/15) wt. % / MEA (a) Top view (500 ×) (b) Cross section view (200 ×)



Fig. 5. Blend membrane of PSU/PVAc (80/20) wt. % / MEA (a) Top view (500 ×) (b) Cross section view (200 ×)

Increasing number of mobile linkages in the polymer backbone increasing the free volume of the polymer when PVAc (rubbery) polymer was used. For PSU (glassy) polymer, to increase polymer free volume through chain backbone packing, the efficiency and cohesive energy density decreased [3, 25]. Morphology of homogenous polymer blend relies upon the composition blend, consistency of the individual segments and the preparation history [23, 26]. The two-stage morphology can altogether impact the pervasion properties of the films. Structures of the developed membranes revealed a packed bed of spheres rather than finger-like microvoids in the sub-porous layer; this indicates the absence of defects and pinholes at the membrane surfaces [3, 27]. Due to the well-known interaction between CO_2 and $-NH_2$ groups, the amine molecules that occupy the micropores will increase the CO_2 adsorption of these materials [23, 24]. In addition, as MEA amine was added, a significant improvement in the membrane's perm-selectivity was also observed. As a consequence of the solubility of CO_2 in MEA amine, the presence of amine enhanced the CO_2 solubility across the membrane. This research into the morphology of different polymer blends with amines was not found in the literature. A. Mushtaq et al.: Synthesis and characterization of polymeric blend membranes enhanced by...

Thermal gravimetric analysis of enhanced polymeric blend membranes

Figure 6 shows the degradation behavior when MEA amine was added in different compositions of PSU/PVAc. The stability of synthesized blend membrane was changed. From this figure for M3 to M6, the primary bend demonstrates the weight reduction of 10 wt. % for MEA at 166.42°C (M3). The second bend shows a mass loss of 5-20 wt. % of PVAc at 326.62°C and the third bend of PSU at 528.32°C demonstrates the 50-60 wt. % mass loss in the blend membranes.

On the contrary, this trend is also shown with M6, degradation onsets at 523.57°C, and maximum degradation temperature is 559.74°C. It is also observed that the amount of residue for all membranes at 800°C has decreased by the addition of MEA and PVAc in PSU. At the end of the degradation, almost 20-25 wt. % of residue

remained. For an effective separation, the polymer should have good interaction with one of the components of the mixture. Molecular structure, arrangement and specific nature of chemical groups attached to the main chain are some factors that affect the properties of the membrane and their performance. In comparison, alkanol amines decompose at a lower temperature than PSU/PVAc because of the substitution of NH group [28, 29]. Table 3 summarized the thermal degradation results.

The degradation products of MEA are mainly formate, hydroxyethyl formamide, hydroxyethyl imidazole and oxalate. Glycolate and acetate are also present, however, in low concentrations. Adding MEA to the blend changed the thermal stability of PSU/PVAc blend. This is probably due to the properties of the amine, specifically its basicity and the number of –OH groups present. These results are in good agreement with previous studies [28-30].



Fig. 6. Effect of TGA on enhanced polymeric blend membranes with various composition of PVAc in PSU with MEA amine

Table 3. Therma	al degradation	temperature	of polymeric	MEA	amine	blend	membranes
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Membran e Sample	PSU wt. %	Polymer B PVAc . wt. %	lend Amine 10wt.%	Degradatio n MEA amine onset temperature (°C)	Maximum MEA amine degradation temperatur e (°C)	Degradatio n onset PVAc temperature (°C)	Maximum degradation PVAc temperatur e (°C)	Degradatio n onset PSU temperature (°C)	Maximum degradation PSU temperatur e (°C)
M1	100	-	-	-	-	-	-	535.13	570.48
M2	-	100	-	-	-	318.54	355.38	-	-
M9	100	-		165.65	200.88	-	-	522.12	543.04
M18	95	5	ME	166.42	178.90	326.62	356.64	528.32	569.44
M19	90	10		164.11	177.56	323.37	355.57	527.76	566.26
M20	85	15	A	163.94	174.06	322.78	352.24	525.50	561.16
M21	80	20		159.74	173.51	320.80	350.63	523.57	559.74

Spectral analysis of enhanced polymeric blend membrane

FTIR spectral analysis of enhanced polymeric blend membranes is shown in Figure 7. A broad

frequency of FTIR spectra for PVAc, PSU, and MEA was examined. A complete spectral analysis was also done to confirm the hydrogen-bonding behavior of the amine blended membranes [38].

Figure 7 shows the FTIR spectra of the synthesized PSU/PVAc/MEA polymeric blend membranes at 10 wt. % MEA with various composition of PVAc in the PSU matrix. The functional groups (S=O, CSO₂C, C-O, C₆H₆, C=O and C-H) of PSU/PVAc blend slightly change their positions, but remain stable in the range. Spectral shifts are observed for the benzene ring by the addition of MEA. The amine group (C-N) appears at 1058.23-1094.71 cm⁻¹ for PSU/PVAc/MEA (M3-M6) blend membranes. The N-H group's peaks for M3 to M6 are observed at 3442.77 cm⁻¹ - 3494.04 cm⁻¹. The hydrogen bonding is a strong intermolecular interface that affects miscibility.

Similarly, by the addition of MEA in the PSU/PVAc blend, the O-H peak appears at 3219.45-3307.86 cm⁻¹ for M3 to M6. Hydrogen bonding is important for hydroxy compounds, but the effect tends to be weaker than for the hydroxy group, and the overall effect on the spectrum is slightly less pronounced. This condition changes the amino salts and related ammonium, where strong hydrogen bonding is experienced, and a consistent broadening of the NH⁺ absorption is observed [31]. This figure shows the incorporation of MEA into PSU/PVAc matrix by confirming the presence of the particular frequency bands of the characteristic peaks which is evidence that the amine had an interaction with the polymer.

The structural differences between different alkanolamine are important, and they strongly influence the chemistry and reactivity of nitrogen and the N-H group. Hydrogen bonding disturbs NH⁺ and OH⁻ groups by altering the electronic field, which then provides the enthalpy that favours mixing [32]. These results indicated that hydrogenbonding interactions existed between the ester carbonyl and carboxyl end groups of PSU and the OH groups of PVAc/amine [23]. Hence, these results of the structural analysis support the compatible nature of PSU/PVAc/amines blend membranes indicated by the microscopic and macroscopic observations.

Polymer blends compatibility, the peak shifts of certain significant bands to other frequencies point to the existence of particular interactions taking place amongst the characteristic groups of the pure PSU/PVAc polymers and amines. The summarized form of different shifts in the FTIR spectra is presented in Table 4 and supports the development of the interactions among the polymers which indicates their miscibility in the form of blended membranes [6, 32-34]. The limited degree of peak shifting revealed by FTIR studies confirmed the miscibility of the tested polymer blends.

Moreover, there was no cross-linking and formation of intermediates, and the frequency shifts observed were peaks that characterized diaryl sulfone, C=O, C-O and N-H groups of PSU/PVAc/amine. These spectral changes point to molecular interactions between the polymer components in the blends, highlighting their compatibility [26]. These observations are in good agreement with previous studies [16, 34, 35].



Fig. 7. Comparative FTIR spectra of the polymeric blend membranes with MEA amine.

Spectral assignment	Wave number, cm ⁻¹	PSU/PVAc/DEA blend membranes Observed wave number, cm ⁻¹	PSU/PVAc/MDEA blend membranes Observed wave number, cm ⁻¹	PSU/PVAc/MEA blend membranes Observed wave number, cm ⁻¹
S=O symmetric stretch	1150-1100	1087.73-1123.15	1105.35-1130.74	1118.13-1140.28
CSO ₂ C asymmetric stretch	1322, 1370-1250	1305.39-1320.16	1307.28-1324.63	1310.93-1334.52
C-O asymmetric stretch	1244, 1260-1000	1057.78-1068.83	1039.92-1052.54	1034.41-1049.26
C ₆ H ₆ ring stretch	1587-1489	1566.80-1585.27	1542.67-1569.39	1570.43-1581.62
OH aliphatic and aromatic stretch	2886, 2938 and 2971	2806.42-2819.88	2871.72-2889.44	2847.29-2867.08
C=O stretch	1736, 1760-1600	1715.21-1722.56	1734.66-1744.27	1730.57-1755.36
C-H phenyl ring substitution band	850, 870-675	802.73-844.06	819.83-867.81	821.52-835.18
C-N stretch	1340-1020	1181.29-1203.19	1207.21-1241.65	1058.23-1094.71
N-H stretch	3500-3300	3488.67-3499.93	3374.21-3378.29	3442.77-3494.04
O-H stretch	3640-3160	3608.18-3625.08	3240.93-3270.11	3219.45-3307.86

A. Mushtaq et al.: Synthesis and characterization of polymeric blend membranes enhanced by... **Table 4.** Summary of the FTIR spectral data of enhanced polymeric blend membranes

CONCLUSION

An enhanced polymeric blend membrane was successfully developed. The morphology of the enhanced polymeric blend membrane showed uniform microspherical structure known as a packed bed of spheres. After addition of amine in the PSU/PVAc polymer blend, the thermal behaviour showed a deviation from the expected trend and the degradation temperature decreased. Furthermore, as MEA amine was added, a remarkable improvement in the membrane's properties was observed. These enhanced polymeric amine blend membranes have a high capability of capturing carbon dioxide from natural gas. In conclusion, the synthesis of EPBM was found to have a promising application for natural gas purification.

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СИНТЕЗ И ОХАРАКТЕРИЗИРАНЕ НА ПОДСИЛЕНИ С МОНОЕТАНОЛАМИН СМЕСЕНИ ПОЛИМЕРНИ МЕМБРАНИ ЗА РАЗДЕЛЯНЕ НА СО₂/СН₄

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(Резюме)

Мембрани за разделяне на газове се използват широко. За ефективно разделяне на CO_2/CH_4 , са необходими високоефективни смесени полимерни мембрани. Основната задача на това изследване е да се синтезират смесени мембрани за отстраняване на CO_2 от CH_4 с помощта на стъкловидни и каучуковидни полимери с добавка на амин. Методологията използва различни съдържания на поливинилацетат (PVAc) от 5 до 20 wt% смесен с полисулфон (PSU) и 10 wt% MEA в разтворител DMA за получаване на плоски филмови мебрани по метода на леене от разтвор. Получените смесени мембрани имат хомогенна повърхност и еднороден слой със сферична структура, както се вижда от FESEM снимките. DSC анализът показва съществуването на еднаква температура на стъкловиден преход за всички полимерни смеси. Термогравиметричният анализ сочи, че максималната температура на деградация се повишава с увеличаване на съдържанието на PVAc в полимерните смеси. Чрез много малкия брой изместени пикове при FTIR анализа е потвърдена смесваемостта на полимерните компоненти. Резултатите за газовата проницаемост в присъствие на MEA показват, че проницаемостта към CO_2 нараства в PSU и PSU 80%/PVAc 20%, съответно от 39.63% на 63.97% при налягане 2 bar. Смесената полимерна мембрана е подходяща за получаване на нови материали с подобрени свойства, които съчетават широки възможности за приложение с ниска себестойност.