

Properties and Characteristic of Amine-Polymer Blend Membrane

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Summary: Polymer blend technology has earned a significant position in the field of polymer science. Current membrane technology can easily and simply remove and separates carbon dioxide as pressure, temperature, costs, and energy requirements are low. There is also no corrosion problem from the straightforward process of removing CO₂ from natural gas, especially in remote or offshore locations that are easily scaled up. However, glassy polymeric membranes suffer from a lack of permeability causing performance degradation and higher selectivity. Nevertheless, amine solutions are capable of purifying naturally acidic gas. Within this framework, the blending of the polysulfone (PSU) glassy polymer with amines such as diethanolamine (DEA), methyl diethanolamine (MDEA), and monoethanolamine (MEA) in a dimethylacetamide solvent, resulted in the development of flat sheet membranes with the desired properties. The findings showed good miscibility between PSU and amines blends, all the original functional groups were shown by FTIR. The synthesized amine polymer blend membrane were found to have homogenous surfaces and a packed bed sphere structure (PBSS) as shown by FESEM images. Furthermore the addition of different amine solution, have increased the size of PBSS due to incorporation of amine molecule into the sphere.

Keywords: Amine-Polymer Blend Membrane, Glassy Polymer, Polysulfone membrane, Diethanolamine, Methyl diethanolamine, Monoethanolamine.

Introduction

Membrane technology has promising potential to facilitate the bulk separation of natural gas from its high carbon dioxide content. For this purpose and to increase carbon dioxide solubility, enhancements have been explored based on polymeric membranes that included the development of (i) mixed matrix membranes; (ii) polymer blend membranes; in addition to (iii) the inclusion of carbon dioxide, solvent like ionic liquids in the polymer blend [1-11]. Polymer blends (PB) comprising a mix of at least one to two polymers with amines have become essential to specific sectors of the polymer industry because they meet specific performance criteria that cannot otherwise be fulfilled by other available products. Hence, their attractiveness is increasing with rising demand [12-14]. In general, blending is the best method for forming significant sites in the membrane matrix. As a consistent significance, numerous studies enthusiastic to polymer matrix stress their thermal and mechanical performance. One is most likely to acquire optimally desired properties by blending amines with miscible polymers. Therefore, it is vital to know exactly which variables influence the miscibility of polymers with amines.

Therefore, homogeneous blends can be preferred as probable membranes for separations as heterogeneous blends, as they do not compromise enough mechanical strength than compared with thin membranes. Homogeneous blends demonstrate a decrease in CO₂ plasticization, as well as contribute

towards improving selectivity CO₂/CH₄ mixtures [15]. The previous studies regarding blend membrane were summarized in Table 1 [6, 16-27]. Blending is a cost and time effective technique to create materials with anticipated properties. Nevertheless, the mixing of rubbery, glassy polymers with amines has not been examined.

In amine polymeric blend membrane fabrication, the appropriate control of morphological development produce the homogeneity that avoids phase separation, which is highly important. Improvements in polymer performance, membrane structure, modular fabrication, and process design have all contributed to increasing the potential range of applications for membranes in natural gas treatment.

Experimental

Materials and Membrane Fabrication

Polysulfone (PSU) Udel® P-1800, with a glass transition temperature (T_g) of 185°C, was attained from Solvay Advanced Polymers; L.L.C, U.S. in powdered form. Diethanolamine (DEA), methyl diethanolamine (MDEA), monoethanolamine (MEA) and dimethyl acetamide (DMAc 99.99% pure) was bought from Merck. Their boiling points: MDEA (247.3°C); MEA (159.6°C); DEA (260°C). The chemical structures of the solvent and amines are shown in Fig 1.

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Table-1: Different studies regarding Polymeric blend membrane.

Year	Polymers	System	Remarks
2002	PI-PES (Glassy-Glassy) coated with PDMS	CO ₂ /CH ₄	High gas permeation
2006	PU based PAI-PEI (Glassy-Glassy) blend	CO ₂	CO ₂ /N ₂ selectivity of PU-based blend membranes was increased
2006	PU-PDMS (Rubbery-Rubbery) cross-linked	CO ₂ /CH ₄	Highest permeability, diffusivity, and solubility values are found for the PDMS membranes
2008	PES-PI (Glassy-Glassy) blend MMM	O ₂ /N ₂	Ideal separation factors of O ₂ /N ₂ is increased
2009	PVAm-PVA with porous PES support	facilitated CO ₂ transport	Ultra-thin membrane with good permeability and selectivity
2010	PEG-PDMS	CO ₂ /CH ₄	Remarkably, the CO ₂ /H ₂ selectivity is enhanced
2011	SPEEK-Matrimid	CO ₂ separation	Cross-linked for anti-plasticization
2011	PSF-PI (Glassy-Glassy)	CO ₂ /CH ₄	studied the effect of solvents
2012	PU-PVAc with PEO-PPO	CO ₂ /CH ₄	increased CO ₂ permeability
2013	PEG-PDMS	CO ₂ /N ₂	Significant improvement in selectivity
2014	CA/TiO ₂ blend	CO ₂ /CH ₄	Permeability of CO ₂ was found to be increased for CA-TiO ₂ blended
2015	PES-PVAc	CO ₂ /CH ₄	CO ₂ permeance increase due to the addition of PVAc in PES
2016	PSF/PI	CO ₂ /CH ₄	Improved selectivity

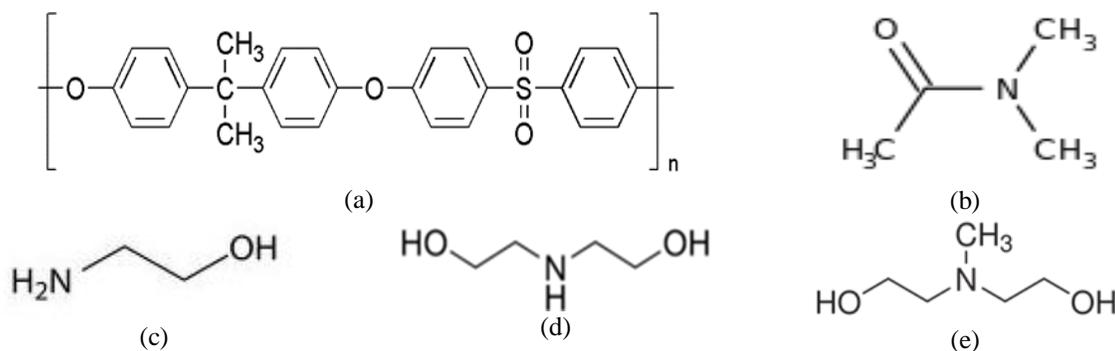


Fig 1: Chemical structure of polymer, solvent and amines (a) PSU (b) DMAc (c) MEA (d) DEA and (e) MDEA.

The amine polymeric membrane (APM) was synthesized by blending the polysulfone with diethanolamine (DEA), methyl diethanolamine (MDEA), monoethanolamine (MEA) was taken in the dimethylacetamide solvent and the dope solution was 20% wt/wt. Polysulfone was preheated for the duration of one night to eliminate moisture. Firstly, the polysulfone was allowable to dissolve completely in dimethylacetamide. After that amine was included with persistent blending for 24 hours. The PSU polymer and amine were dissolved in the solvent at room temperature under constant blending to acquire a homogeneous outcome. To obtain a clear solution (remove air bubbles), followed by bath sonication in Transonic Digital S, Elma® for 3 hours at a frequency of 100 Hz. Polysulfone and amine were completely dissolved without any evidence of deposition, which qualified it as a miscible polymer blend. The blend was then cast on a glass plate via casting knife (with an opening of 200µm). The casted membranes were sited in a drying room at ambient temperature for five days to allow for the evaporation of the solvent. The membranes were then peeled off

from the glass plate for characterization. Table 2 illustrate the composition of the polymer blended membranes.

Table-2: Composition of amine polymeric blend membranes.

Membrane	PSU polymer wt.%	Amine 10 wt.%
M1		-
M2	100%	MEA
M3		DEA
M4		MDEA

The casted amine-polymer blended membranes (APMs) were analyzed for surface and cross-sectional morphology as well as weight loss. Field emission electron scanning microscopy (FESEM instrument, SUPRA thru ZEISS model 55VP) was used, and Thermogravimetric Analysis (TGA; model Perkin Elmer, TGA-7) were also carried out at temperatures ranging from 28–800°C at a heating rate of 10°C.min⁻¹. Fig 2 show the methodology for fabrication of amine polymer blend membrane.

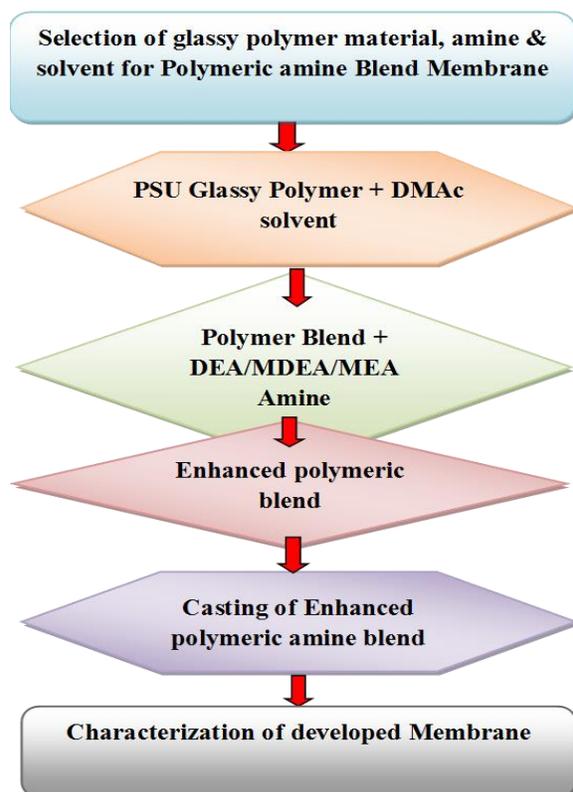


Fig 2: Methodology for fabrication of polymeric amine blends membrane.

Results and Discussion

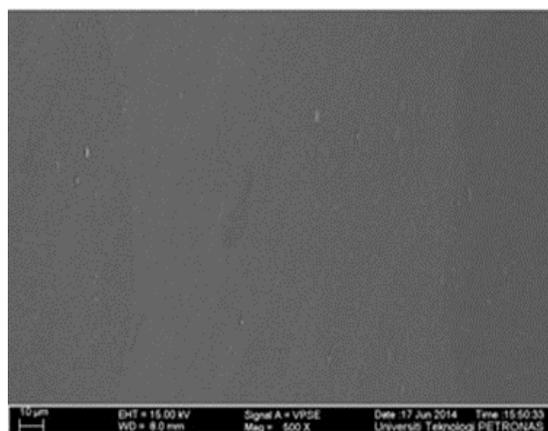
Morphology of Polymeric Amine Blend Membrane

The morphology by FESEM images shown in Figs 3 and 4 demonstrate the morphology of based PSU and PSU with different amines. Fig 3(a) shows the surface of a based PSU membrane making it clear

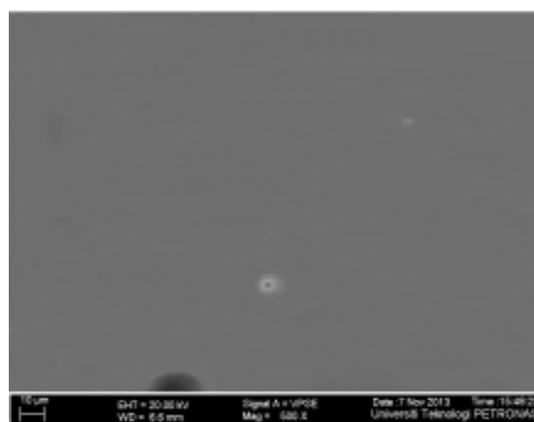
that a dense surface was effectively synthesized. The surface view reveals no pores and the dense structure of the PSU is confirmed by the image [1]. Figs 3(b) (PSU/DEA 10 wt. %); 3(c) (PSU/MEA 10 wt. %); and 3(d) (PSU/MDEA 10 wt. %) show surfaces of the blended membranes which were uniformly without any signs of phase separation, thus confirming the miscibility of the polysulfone with amines [3].

Similarly, compare a cross section of based polysulfone membrane with the blended membranes, [See Fig 4(a)] demonstrate microporous structure known as packed bed of spheres, which were uniformly distributed [28]. Since PSU backbone possesses the polar $-\text{SO}_2-$ groups and rigid aromatic rings, it had caused the structure to be very rigid; chain motion is restricted to bond vibrations and coagulative. Due to higher viscosity, such type of structure is formed in PSU membrane which is reported in the previous works which is also consistent with the literature [29].

Figs 4 (b) PSU/DEA 10 wt. %; 4 (c) PSU/MEA 10 wt. %; and 4 (d) PSU/MDEA 10 wt. %; also show that the blended membranes presented highly packed uniform structures. The cross-sections show excellent blended interaction with symmetrical microporous structures between the PSU polymer and DEA, MEA and MDEA amines. Amines can be radically enhanced by incorporating disparities in the basic structure of a PSU polymer. Shape and size of the bulky groups in principle chain and additionally the side chain change the essential properties like rigidity and packing density, which in turn effect its accessibility [1].



(a)



(b)

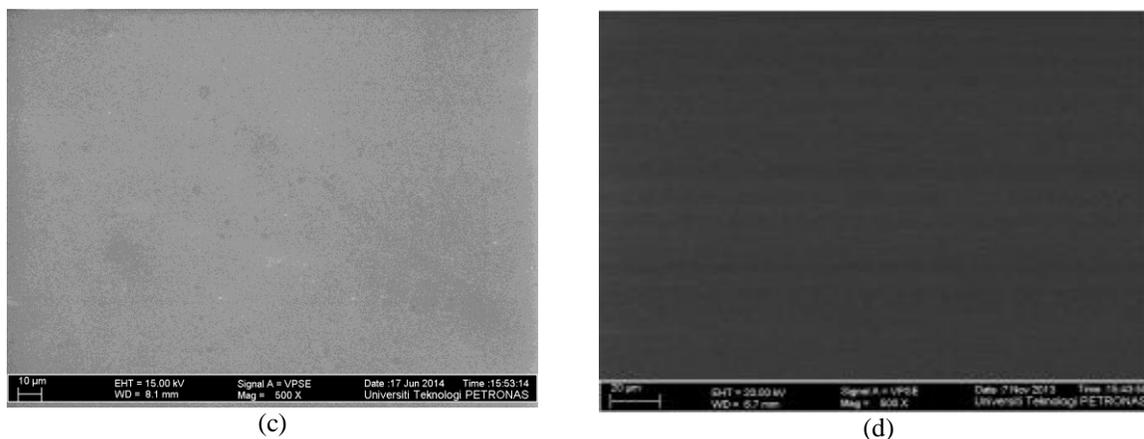


Fig. 3: Top view of membranes (500X) (a) Based PSU (b) PSU/DEA 10 wt. % (c) PSU/MEA 10 wt. % (d) PSU/MDEA 10 wt. %.

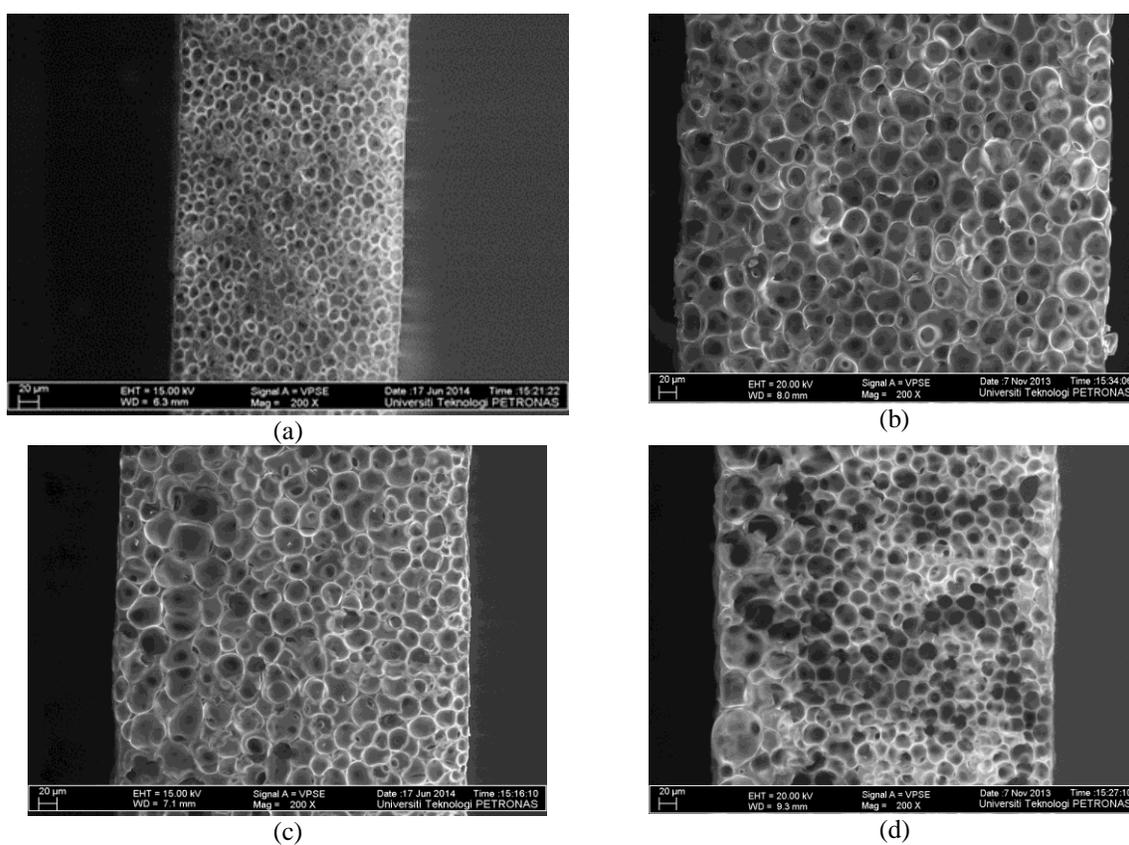


Fig. 4: Cross-section view of membranes (200X) (a) Based PSU (b) PSU with DEA 10 wt. % (c) PSU with MEA 10 wt. % (d) PSU with MDEA 10 wt. %

When an amine is added to the casting solution, its thermodynamic stability is changed and can affect the solvent exchange rate, resulting in kinetic effects. According to the literature, amines with different structures exert different effects on the properties of the membrane. These effects are due to

the attraction of the amine to the polymer chains and its affinity for the solvent. These effects are important for ethanolamines with OH^- or $-\text{NH}^+$ functional groups [30]. For instance, the presence of these hydrophilic functional groups in the casting solution

increases the affinity and the exchange rate of diffusion through the membrane.

In general, using amines increases the viscosity of the casting solution, which has significant thermodynamic and kinetic effects. The physical structure of this membrane incorporates the mechanical condition of matter (order, density, and mobility) has a robust behaviour on gas separation properties of CO₂ and CH₄. This variation in the size of packed bed of sphere structures was due to change of fundamental property of amine like density [1]. Hence, the dependence of permeability on the chemical structure can only be an uneven estimate, since the chemical structure is the main factor for evaluating membrane properties [31-35]

Thermal Gravimetric Analysis of Polymeric Amine Blend Membrane

Thermal Gravimetric Analysis describes the thermal degradation temperature of a polymer. TGAs for the blended membranes are shown in Fig 5. The pure PSU membrane was synthesized in DMAc, and polymer degradation was initiated at 535.13°C and continued until 570.38°C. Polysulfone suffers thermal decomposition to give various decomposition products, which including alkenes and sulfur dioxide. Weakest bond in a polysulfone chain is the C-S bond due to C-O bond [36]. Adding DEA, MEA and

MDEA to PSU changed its thermal stability. For PSU with DEA 10 wt. %, degradation ranged from 510.82 to 542.71°C. For PSU with MEA 10 wt. %, degradation ranged from 522.12 to 543.04°C. For PSU with MDEA 10 wt. %, degradation ranged from 505.68 to 551.11°C. Oxidative degradation products can contribute to amine losses, impact system economics, create environmental impacts and contribute to further amine degradation [37, 38]. The adding of MEA/DEA/MDEA to polysulfone, blend seems to have rehabilitated the thermal stability [37-39]. According to the literature, amines with different structures exert different effects on the properties of the membrane. These effects are due to the attraction of the amine to the polymer chains. These effects are important for amines with -OH or -NH functional groups. At the end of the degradation, almost 20-25 wt. % residual remained.

Spectral Analysis of polymeric amine blend membrane

A complete spectral analysis was also done to confirm the hydrogen-bonding behaviour of the blended membranes. Various vibrational modes and probable assignments are discussed below with Table 3 showing spectra for the functional groups observed.

Table-3: Summary of the FTIR spectral of PSU and polymeric membrane with amines.

Spectral Assignment	Wave number cm ⁻¹	PSU/DEA blend membranes	PSU/MDEA blend membranes	PSU/MEA blend membranes
		Observed wave number cm ⁻¹	Observed wave number cm ⁻¹	Observed wave number cm ⁻¹
S=O symmetric stretch	1150-1100	1128.05	1121.41	1124.57
CSO ₂ C asymmetric stretch	1322, 1370-1250	1322.19	1319.36	1327.22
C-O asymmetric stretch	1244, 1260-1000	986.67	991.28	996.24
C ₆ H ₆ ring stretch	1587-1489	1575.90	1578.21	1581.37
OH aliphatic and aromatic stretch	2886, 2938 and 2971	2884.82	2881.63	2879.51
C-N stretch	1340-1020	1207.30	1184.91	1195.76
N-H stretch	3500-3300	3447.47	3418.15	3436.84
O-H stretch	3640-3160	3640.92	3657.66	3640.14

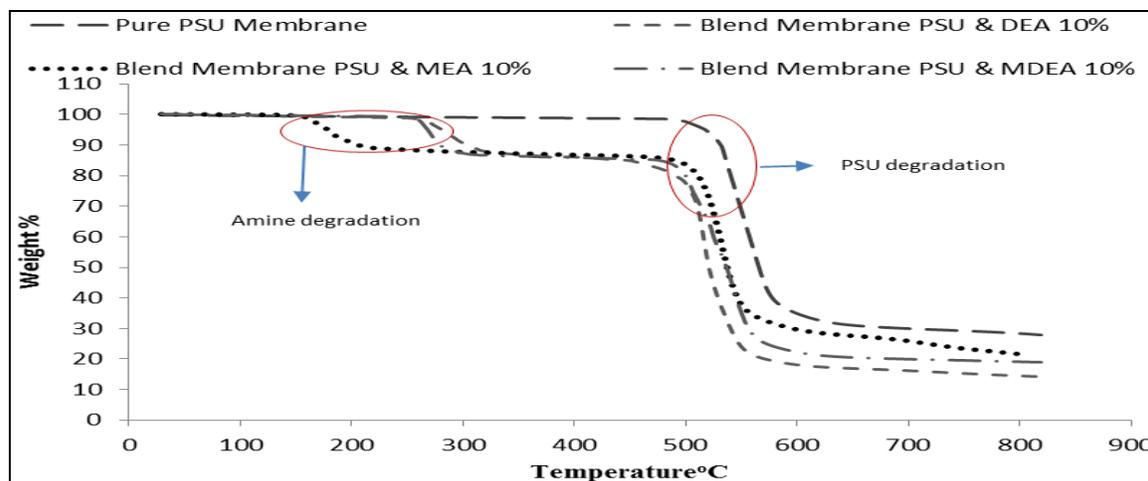


Fig. 5: Effect of thermal gravimetric analysis on polymeric amine blend membranes.

FTIR investigations of miscible blends not only reveal the existence of component interactions but provide data describing component groups. Fig 6, shows the FTIR for based PSU with the subsequent functional group S=O, CSO₂C, C-O, C₆H₆ and the OH aliphatic and aromatic stretch. In based PSU, the sulfone S=O group was symmetric wave number is 1150.00cm⁻¹; the peak shifted to 1125.89 cm⁻¹ without any large change because of vibration stretching. The CSO₂C asymmetric stretch peak faintly shifted to 1323.53cm⁻¹ attributable to hydrogen bonding. The C-O asymmetric stretch peak in polysulfone (1244cm⁻¹) moved to 1018.45cm⁻¹ because of hydrogen shift bonding [40]. The C₆H₆ ring stretch (wave number 1587.00cm⁻¹) peaked at 1579.33cm⁻¹ as a slight change however generally stayed stable. The OH aliphatic stretch (wave number 2886.00cm⁻¹) band arisen at 2880.15cm⁻¹ as a result of weak electro-negativity of the hydroxyl ion.

Figs 7, 8 and 9 show FTIRs for the polymeric membranes (PSU with amines: DEA, MDEA, and MEA). Sulfone group (S=O, symmetric in PSU) wave number (1150.00cm⁻¹) shifted its peaks to 1128.05cm⁻¹, 1121.41cm⁻¹, and 1124.57cm⁻¹, respectively, due to vibrational stretching. The CSO₂C asymmetrical stretch peak shifted slightly to 1322.19cm⁻¹, 1319.36cm⁻¹, and 1327.22cm⁻¹, respectively, caused by hydrogen bonding. The C-O asymmetric stretch peak (wave number 1260-1000cm⁻¹) moved to 986.67cm⁻¹, 991.28cm⁻¹ and 996.24cm⁻¹ caused by hydrogen bond shifted. The

C₆H₆ benzene ring stretch peak (wave number 1587cm⁻¹) occurred at 1575.90cm⁻¹, 1578.21cm⁻¹, and 1581.37cm⁻¹, respectively. The OH aliphatic stretch band was at 2884.82cm⁻¹, 2881.63cm⁻¹, and 2879.51cm⁻¹, respectively, because of the weak electro-negativity of the hydroxyl ion. In Figs 7, 8 and 9, the amine group, C-N, appears at 1207.30cm⁻¹, 1184.91 cm⁻¹ and 1195.76cm⁻¹, correspondingly. The OH group in amine appears at 3640.92cm⁻¹, 3657.66cm⁻¹ and 3640.14cm⁻¹, respectively, because of the electronegativity of the hydroxyl group. The N-H group peaked occurred at 3447.47cm⁻¹, 3418.15cm⁻¹ and 3436.84cm⁻¹, respectively, caused by vibrations reflecting hydrogen bonding of the amide groups [41]. Due to N-H group, the formation of hydrogen bond usually, shifts to a lower frequency. This is a vital source of facts, as hydrogen bond formation is a strong intermolecular interface that influences miscibility.

The occurrence of hydrogen bond interactions perturbs OH⁻ and NH⁺ groups by changing the electronic environment, thus, providing advantageous enthalpy for the process of mixing. While a self-associating polysulfone molecule is a constituent of the mixture than the enthalpy of hydrogen bond formation is always negative. However, a positive influence causes an enthalpy change rises from the breach of hydrogen bonds from self-associating molecules [42].

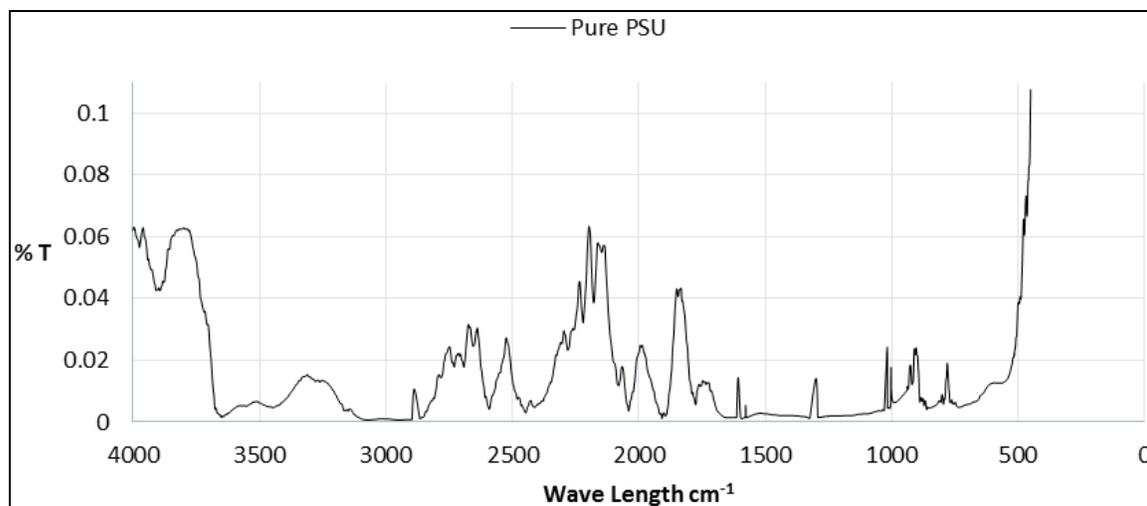


Fig. 6: FTIR graph of polymeric membrane of PSU.

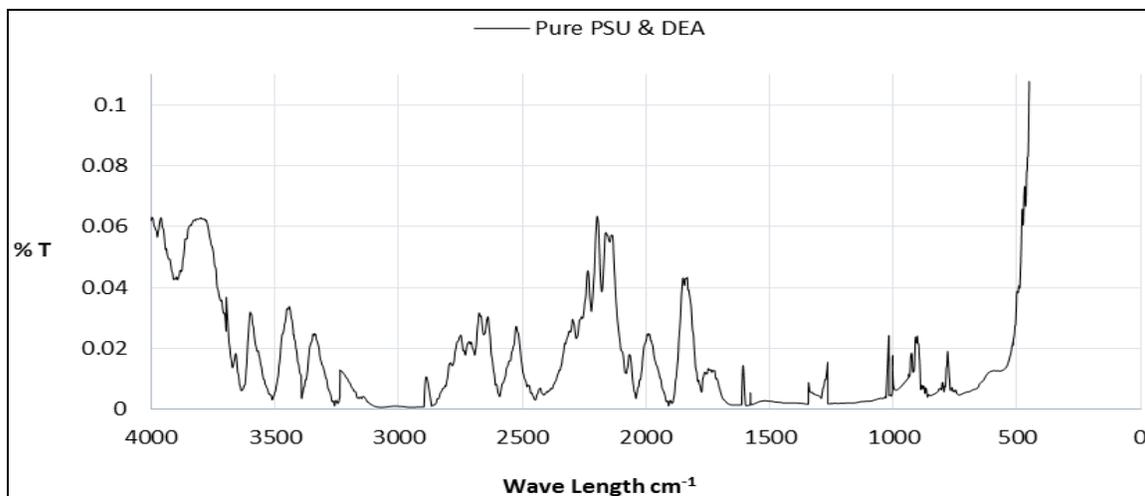


Fig 7: FTIR graph of polymeric amine blend membrane of PSU and DEA 10 wt. %.

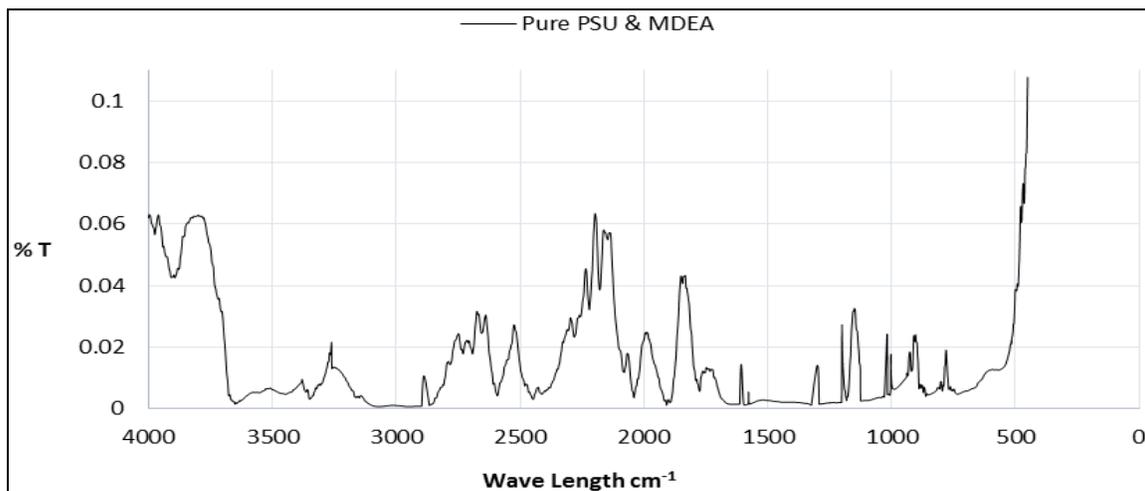


Fig. 8: FTIR graph of polymeric amine blend membrane of PSU and MDEA 10 wt. %.

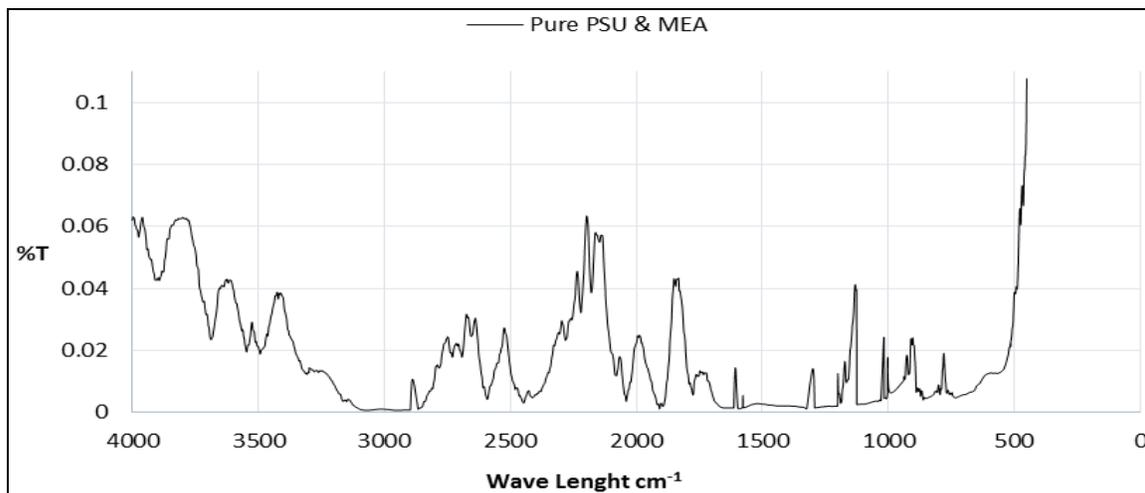


Fig. 9: FTIR graph of polymeric amine blend membrane of PSU and MEA 10 wt. %.

Conclusion

The blending of polysulfone with amines has proven appropriate for the creation of novel materials that combine characteristics which collectively improve applicable properties with lower costs in material performance. Top and cross-section view of based PSU and PSU with amines shown good molecular interactions confirming the miscibility of the polymer. FTIR results provided data on intermolecular hydrogen bonding that favoured. The thermal behaviour of PSU-amine polymers demonstrated a difference from the expected trend in which degradation temperatures dropped. Alkanolamine MEA, DEA, and MDEA are commonly used for CO₂ removal. In this research Polymeric Blend complexes in alkanol amine solution to incorporate the MEA, DEA and MDEA molecules into the pores of the aforesaid microporous membrane. The amine molecules that possess the micropores will build the carbon dioxide adsorption of these materials because of the well-known interaction between carbon dioxide and –NH₂ groups. Moreover, as MEA, DEA and MDEA amine was added a remarkable improvement in the membrane performance. Furthermost, soluble nature of CO₂ in MEA, DEA and MDEA, improved CO₂ solubility through the membrane. Future investigations will include the addition of inorganic fillers as carbon molecular sieves; as well as zeolites that will further enhance the polymeric blended membrane.

NOMENCLATURE

CA	Cellulose acetate
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infra-red
PAI	Polyamide imide
PDMS	Polydimethylsiloxane
PEA	Aromatic polyether amide
PEG	Polyethylene glycol
PEI	Polyetherimide
PEO	Polyethylene oxide
PES	Polyether sulfone
PI	Polyimide
PIM-1	Polymer of intrinsic microporosity
PPO	Polypropylene oxide
PU	Polyurethane
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
PVAm	Polyvinyl amine
PVDF	Polyvinylidene fluoride
PVP	Polyvinyl propylene
SPEEK	Sulfonated aromatic poly(ether-ether-ketone)
TGA	Thermal Gravimetric Analysis

Formulas

C-O	Ketone
C ₆ H ₆	Benzene
C-N	Amine
CSO ₂ C	Dimethylsulfone
N-H	Amide
O-H	Hydroxyl
S=O	Sulfone

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