

## CHARACTERIZATION OF SYNTHESIZED POLYMERIC BLEND MEMBRANES ENHANCED BY METHYL DIETHANOLAMINE FOR EFFICIENT CO<sub>2</sub> SEPARATION

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### ABSTRACT

The limited performance of pure glassy and rubbery polymeric membranes for natural gas purification are due to their intrinsic properties. Optimizing their properties by blending both polymers are expected to address the shortage. The foremost objective of this research is to synthesis enhance polymer blend membranes (EPBM) using glassy polysulfone (PSU) and rubbery polyvinyl acetate (PVAc) with the addition of amine for carbon dioxide (CO<sub>2</sub>) removal from methane (CH<sub>4</sub>). The EPBM were developed by varying the composition of PVAc ranging from 5 to 20 wt. % with 95 to 80 wt. % base PSU in dimethylacetamide (DMAc) solvent. The amines composition was added to the blend and kept at 10 wt. % over solvent. The findings showed good miscibility between PSU and PVAc blends and the original functional groups of polymers and amines were shown by FTIR with very few spectral peak shifts. The synthesized EPBM were found to have homogenous surfaces and a packed bed sphere structure as shown by FESEM images. Increasing the composition of PVAc from 5 to 20 wt. % has significantly reduced the glass transition temperature ( $T_g$ ) of PSU from 185.09°C to 155.75°C.

**Keywords:** Carbon Dioxide, Methyl Diethanolamine, Polymeric Blend Membranes, Polysulfone, Polyvinyl Acetate

### INTRODUCTION

The most corporate contaminant of natural gas is carbon dioxide and it must be removed to a minimum level of less than 2% to minimize pipeline corrosion. Until the overview of membrane technology, standard removal techniques utilized amine absorption. Membranes are the technology of best for CO<sub>2</sub> removal systems for offshore platforms and are even beginning to compete head-to-head with amine structures at onshore plants. Membrane systems are skid mounted, so that scope, time and cost taken for site preparation are minimized. Installation costs are considerably lower than other technologies, particularly for offshore locations. Moreover, for water treatment and solvent storage no additional facilities are needed. Pure glassy and rubbery polymeric membranes are problematic in natural gas purification due to its physicochemical characteristics. The rubbery polymeric membranes are soft and flexible, also they operate above  $T_g$  with high permeance, but low selectivity, whereas glassy polymeric membrane are rigid and operate below  $T_g$  with low permeance but high selectivity. The CO<sub>2</sub> interact more vigorously with rubbery polymers and exhibit high solubility [1-6].

With the purpose of optimize the benefits of both polymers, blending of glassy with rubbery polymers improve membrane properties for gas separation. Although, the polymeric blend membranes has many advantages in terms of thermal, chemical stability permeability and selectivity. To enhance the compatibility of polymer blend, a third component is added such as alkanolamine. It is expected that the addition of alkanolamine will improve the PBM properties as well as the gas separation performance [7-10].

Amine solutions help purify acidic natural gas. Alkanolamine removes CO<sub>2</sub> from a gas stream via an exothermic reaction between CO<sub>2</sub> and the functional group of amine in alkanol amine. Amine addition to the polymer blend may affect the polymer's capacity for absorption, and thus, allow enhanced permeability[11-13]. In EPBM fabrication, the appropriate control of morphological development obtains the homogeneity that avoids phase separation, which is highly important. EPBM fabrication proceeds with PSU-PVAc blended with different amines in a suitable solvent. Thus, by blending glassy with rubbery polymer using amine solution, the properties of membrane was also enhanced for the CO<sub>2</sub>/CH<sub>4</sub> separation [14].

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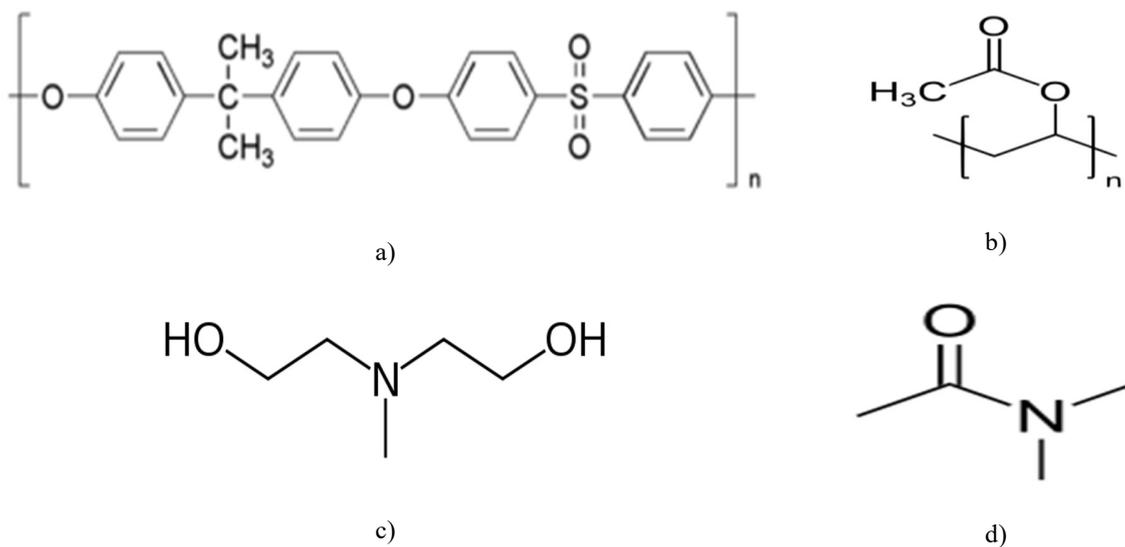
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## METHODOLOGY

### Materials and Method for Membrane Fabrication:

Rubbery and glassy polymers were used to fabricate polymeric membrane films. The polysulfone (PSU) Udel® P-1800 was a powdered grade, glass transition temperature ( $T_g$ ) of 185°C was assimilated from Solvay Advanced Polymer; L.L.C, U.S. The polysulfone PSU polymer was selected mainly due to its ease of fabrication, good properties like high strength and good thermal stability associated with low cost and ease of availability. This material also offers very good control of pore size, pore size distribution, and good film-forming properties.

The polyvinyl acetate (PVAc) average molecular weight  $M_w \sim 100,000$  beads were purchased from Sigma-Aldrich, Germany with a glass transition temperature ( $T_g$ ) of 28°C. PVAc was selected due to its flexible strong bonding and non-acidic nature. The chemical structures of the both polymers are shown in Figure 1 [15-17]. The membrane structure and its performance are mostly affected by the selection of suitable solvent. After reviewing the literature on the solubility of PSU and PVAc polymers, dimethylacetamide (DMAc) solvent was selected by its properties. A dimethylacetamide (DMAc) solvent and methyl diethanolamine (MDEA) 99.99% pure was acquired from Merck, Germany. The chemical structures are shown in Figure 1 [16, 18, 19].



**Figure 1.** Chemical structure a) polysulfone, b) polyvinyl acetate, c) methyl diethanolamine, d) dimethylacetamide

The polymer blend membrane was synthesized with different composition of PVAc and PSU in DMAc solvent. Firstly PVAc was dissolved in the DMAc solvent completely. At that time PSU polymer and MDEA amine was added. Stirring was continuous for 24 hours. Polymers and amine were dissolving in the solvent under continuous stirring at room temperature to get a homogeneous mixture. This blend commonly raised as the casting solution was synthesized by dissolving 20 wt. % of polymer in the DMAc solvent to develop membranes with different compositions. To remove air bubbles form during blending the solution was allowed to immersion sonication in Transonic Digital S, Elma® for 3 hours at a frequency of 100 Hz. Each polymer and amine was fully dissolved in the solvent and there were no signs of agglomeration upon erect the solution which showed that it was a miscible blend. This casting solution was cast on a glass plate with the help of 200 $\mu$ m opening casting knife. After 1 hour of evaporation, the film was dried in an oven at 70°C for 2 hours. These cast membranes were then drying in a room temperature for five days. These synthesized membranes were unpeeled from the glass plate for characterization (description). The configurations of synthesized polymeric blend membrane be present given in Table 1.

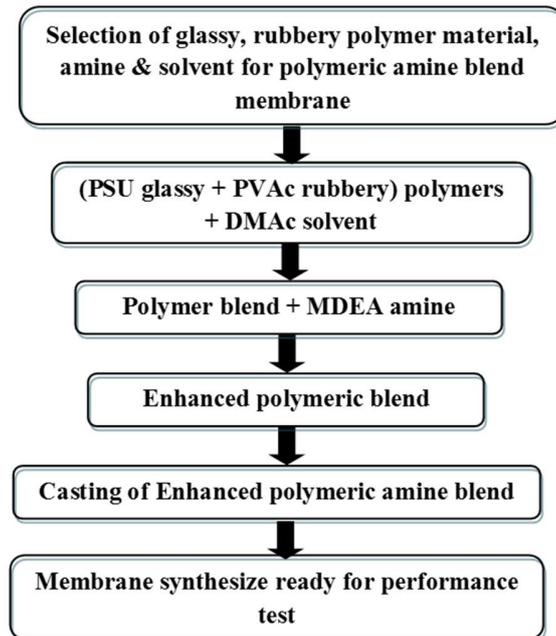


Figure 2. Research approach

Table 1. Different composition of polymeric blend membranes in DMAc solvent

Membrane	Polymer wt. %		Amine 10% wt. %
	PSU	PVAc	
M1	100%	0%	-
M2	0%	100%	
M3	95%	5%	MDEA
M4	90%	10%	
M5	85%	15%	
M6	80%	20%	

### Field Emission Scanning Electron Microscope (FESEM)

The membrane morphology (pore size distribution) of the polymer membrane, polymer blend membrane, amine polymer membrane and enhanced polymeric amine blend membrane were studied by Field Emission scanning Electron microscope (FESEM) instrument, SUPRA by ZEISS model 55VP. FESEM micrographs provide a qualitative assessment of membrane morphology and the homogeneity throughout the polymer matrix. The Supra55VP FESEM allows surface examination down to nanometer scales in either Variable Pressure (VP) model or high vacuum model and provide magnifying 2K to 10K. To characterise the membrane film, the films were initially fractured cryogenically in liquid nitrogen, to get a clear cut of the cross section and mounted onto a circular stainless steel sample holder with an electrically conductive double sided tape. Immersing membrane film for several minutes in liquid nitrogen was necessary for the less brutal membrane. FESEM micrographs were examined using an accelerating voltage of 5kV with magnification; the surface view was at 500 X and cross section view 200 X.

### Thermal Gravimetric Analysis (TGA)

The Perkin Elmer TGA 7 Thermogravimetric analysis was used to determine the amount and rate of change in the sample weight as a function of time or temperature under controlled conditions. These measurements were

mainly worked to measure the thermal stability of a material and compositions of their products along with used precursors. The TGA of the blended membranes sample, weighing about 10-15mg were run from ambient to 800°C at 10°C/min varying heating rate of 20mL/min under a nitrogen atmosphere.

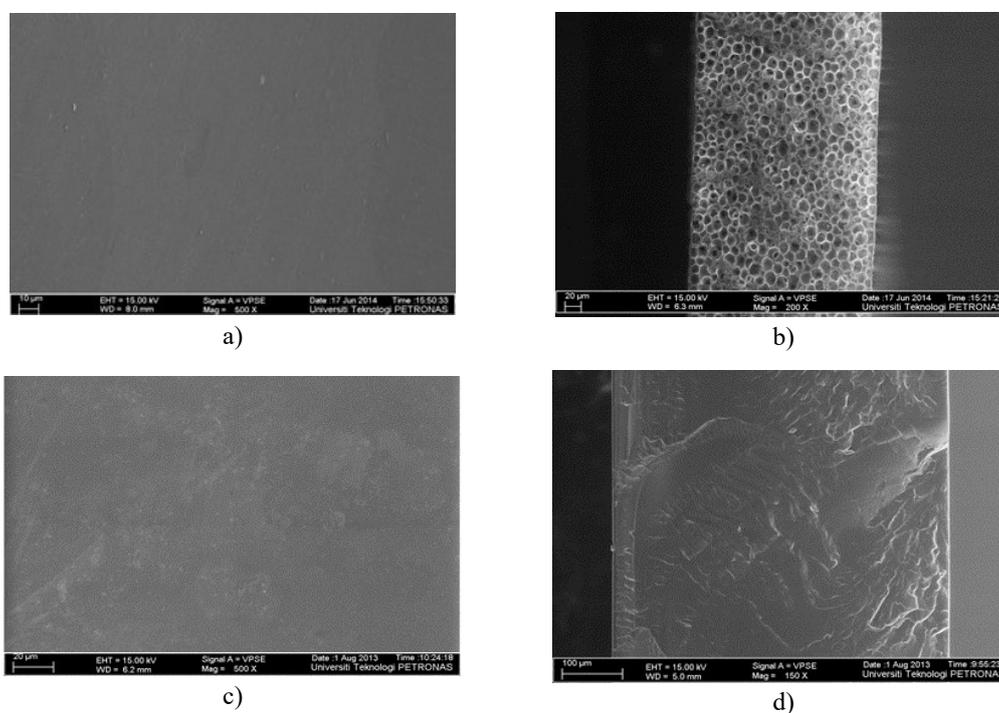
### Fourier Transform Infrared Spectroscopy (FTIR)

Perkin Elmer Spectrum One FTIR Spectrometer was used to determine the functional group present in a molecule by observing the specific absorption of radiation by each molecule in the sample. FTIR analysis of developed polymeric blend membranes was examined the interaction between two polymers and amines. The scans were 20 with wavelength range  $4000\text{cm}^{-1} - 450\text{cm}^{-1}$  and spectra were gotten from a sampling area, diameter 200-micrometer. The samples from the membrane were cut at random positions from developed membranes and then clamped to the plate. Using equipment software, the all spectra were rectified for the FTIR characteristic progressive rise in the absorbance at lower the wave numbers. The wavelength or the frequency of absorption rely on the relative mass and geometry of the atoms and the constant force between the bonds.

## RESULTS & DISCUSSION

### Morphology of Synthesized Enhanced Polymeric Blend Membranes

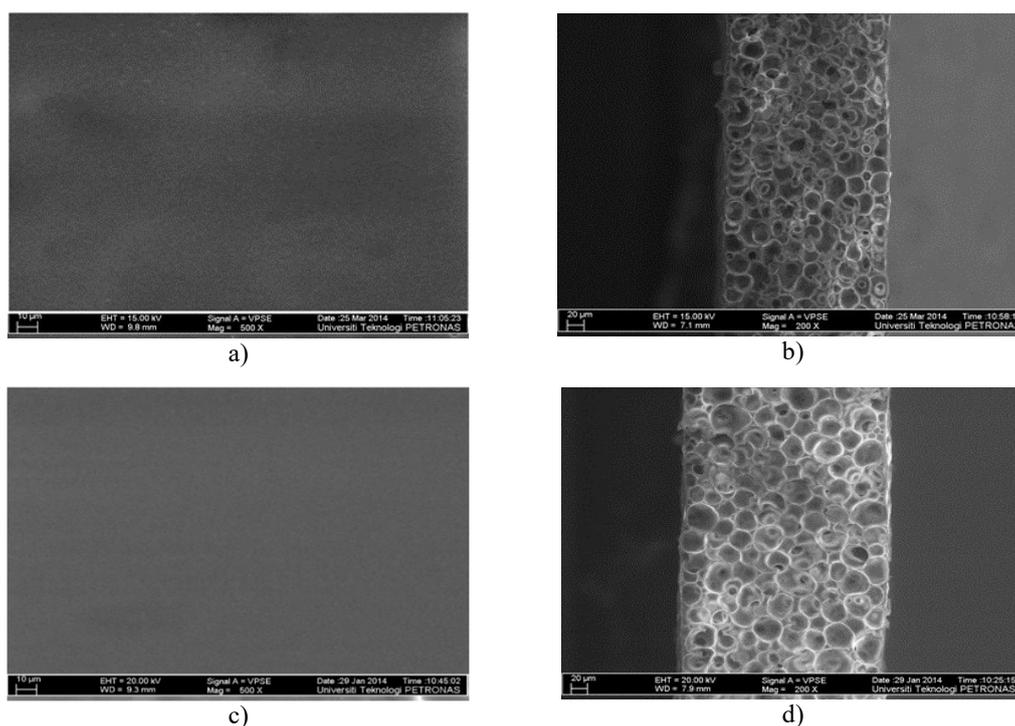
The FESEM morphology of the top and cross-section view of PSU/PVAc/MDEA blend membranes with based polymeric membranes were compared. Figure 3 (a) shows that there were no microvoids, seen on the PSU surface. The cross section of based PSU membrane indicates that microporous structure was uniformly distributed with the sphere structure size of  $16.68 \pm 3.35\mu\text{m}$  as illustrated in Figure 3 (b). This type of structure is known as packed bed of spheres [20]. Since PSU possesses the polar  $-\text{SO}_2-$  groups and rigid aromatic rings, caused the structure to be very rigid, chain motion is restricted to bond vibrations and coagulative, lead to the higher viscosity of casting solution [21]. Due to higher viscosity, such type of structure is formed in PSU membrane which is in accordance with the previous works [22].



**Figure 3.** a) Top view (500 X), b) cross section view (200 X) of PSU based membrane and c) top view (500 X), d) cross section view (200 X) of PVAc based membrane

The FESEM morphology of the based PVAc membrane is shown in Figure 3 (c). There was no crack or defect observed on the surface, resulting in a dense homogenous polymeric membrane. Figure 3 (d) shows that the PVAc possesses dense structure due to the absence of crystallinity, paucity of polar groups, and low degree of crosslinking. As a result of the presence of C=O polar bonds of carbonyl groups in polyvinyl acetate and the phase behavior of CO<sub>2</sub> exposed in polyvinyl acetate, leads to higher solubility of CO<sub>2</sub>.

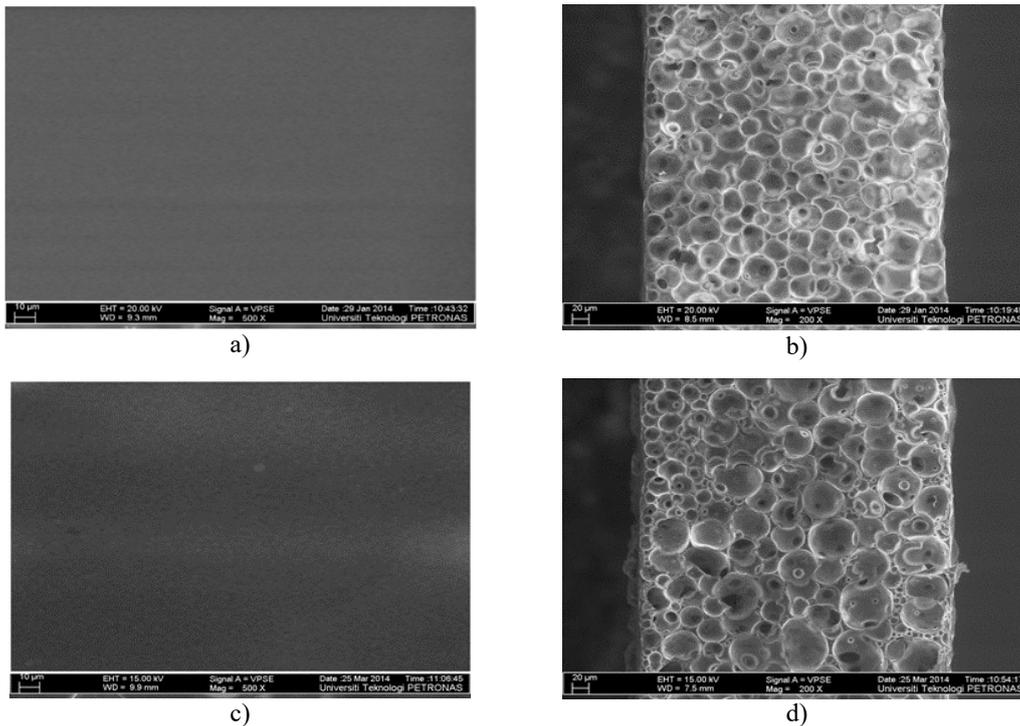
Figure 4 and 5 shows the morphology of PSU with different compositions of PVAc and MDEA 10 wt.% blended membrane. The top view of Figures 4 (a, c) and 5 (a, c) shows that membrane was effectively synthesised without any crack or defect. Their surfaces were uniform which affirmed the miscibility of both polymers with MDEA amine.



**Figure 4.** a) Top view (500 X), b) cross section view (200 X) of blend membrane PSU 95% / PVAc 5% / MDEA and c) top view (500 X), d) cross section view (200 X) of blend membrane PSU 90% / PVAc 10% / MDEA

Correspondingly, on comparing cross-sections: Figures 4 (b, d) and 5 (b, d) the blended polymeric membranes were highly packed with a uniform packed bed of sphere but the size was somewhat different due to different compositions of PVAc. For PSU/PVAc (95/5) and 10% MDEA the microspheres size watched is  $29.62 \pm 9.7 \mu\text{m}$ , for PSU/PVAc (90/10) and 10% MDEA the structure size got to be  $34.57 \pm 6.56 \mu\text{m}$ . Furthermore, when 15% PVAc was included in PSU with 10% MDEA the packed bed of sphere size is  $39.70 \pm 9.89 \mu\text{m}$ , as 20% PVAc was included the sphere size is  $56.15 \pm 10.64 \mu\text{m}$ . Although various creations of PVAc, vinyl acetate derivation in PVAc has been ascribed to its huge free volume, which might be because of the adaptability of the vinyl acetate linkages in the polymer [23]. Alkanolamines arrangement consolidates the amine atoms into the aforesaid materials. These cross-sections show well-blended interaction with microstructures between the PSU/PVAc polymers and MDEA amine.

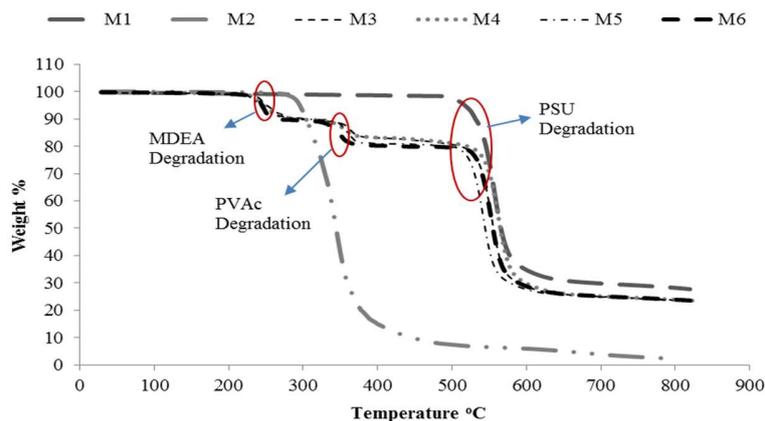
The sphere size changes due to the increasing composition of PVAc. As vinyl acetate in PVAc has been accredited to its large free volume, cause due to the flexibility of the vinyl acetate linkages in the polymer chain [24]. Amine molecules dispersed in PSU/PVAc matrix. The most common specific intermolecular interactions occurring between polymer chains and amine are hydrogen bond, hydroxyl bond, ionic bond, and dipole-dipole interactions [25].



**Figure 5.** a) Top view (500 X), b) cross section view (200 X) of blend membrane PSU 85% / PVAc 15% / MDEA and c) top view (500 X), d) cross section view (200 X) of blend membrane PSU 80% / PVAc 20% / MDEA

### Thermal Gravimetric Analysis of Enhanced Polymeric Blend Membranes

Figure 6 represents the TGA graph of based PSU and PVAc membranes, respectively. This figure shows that the PSU started to degrade at 535.13°C and thermal degradation ends on 570.48°C. At these points, the polysulfone undergoes thermal decomposition that affords a variety of decomposition products including sulfur dioxide and alkenes. The weakest bond in a polysulfone chain is the C-S bond, due to the C-O bond [26].



**Figure 6.** Effect of TGA on enhanced polymeric blend membranes with various composition of PVAc in PSU with MDEA amine

The PVAc membrane-initiated to degrade at 318.54°C, and 355.38°C is the final degradation temperature. The mechanism of thermal degradation of polyvinyl acetate is a complex process including, among other, radical

recombination, the chain fission, carbon-hydrogen single bond fission, radical addition and abstraction mild chain end chain scission. It also includes disproportionate conjugated double bond and hydrogen transfer formation a fusion of aromatic ring, aromatization, cyclisation, graphitization reactions and char formation [27, 28]. This figure also shows that the thermal degradation behaviour of enhanced polymeric blend membranes with MDEA amine. The adding MDEA 10 wt. % to PSU/PVAc polymer blend, altered the thermal stability of both polymers. This figure shows for the M3 membrane, the constancy of the resultant blend changed to 533.29°C for PSU. Correspondingly, this trend was also similar for M4, M5, and M6 blend membranes. For M6, degradation onsets at 525.07°C and maximum degradation temperatures of 557.43°C. The PSU chain contains C-O bond and PVAc acetate group which interact OH group at low temperature on polymer side chains, followed by the breakdown of the polymer's backbone at higher temperatures [27, 29]. Table 2 summarises thermal degradation results.

**Table 2.** Summary of thermal gravimetric degradation temperature ( $T_g$ ) of enhanced polymeric blends membranes

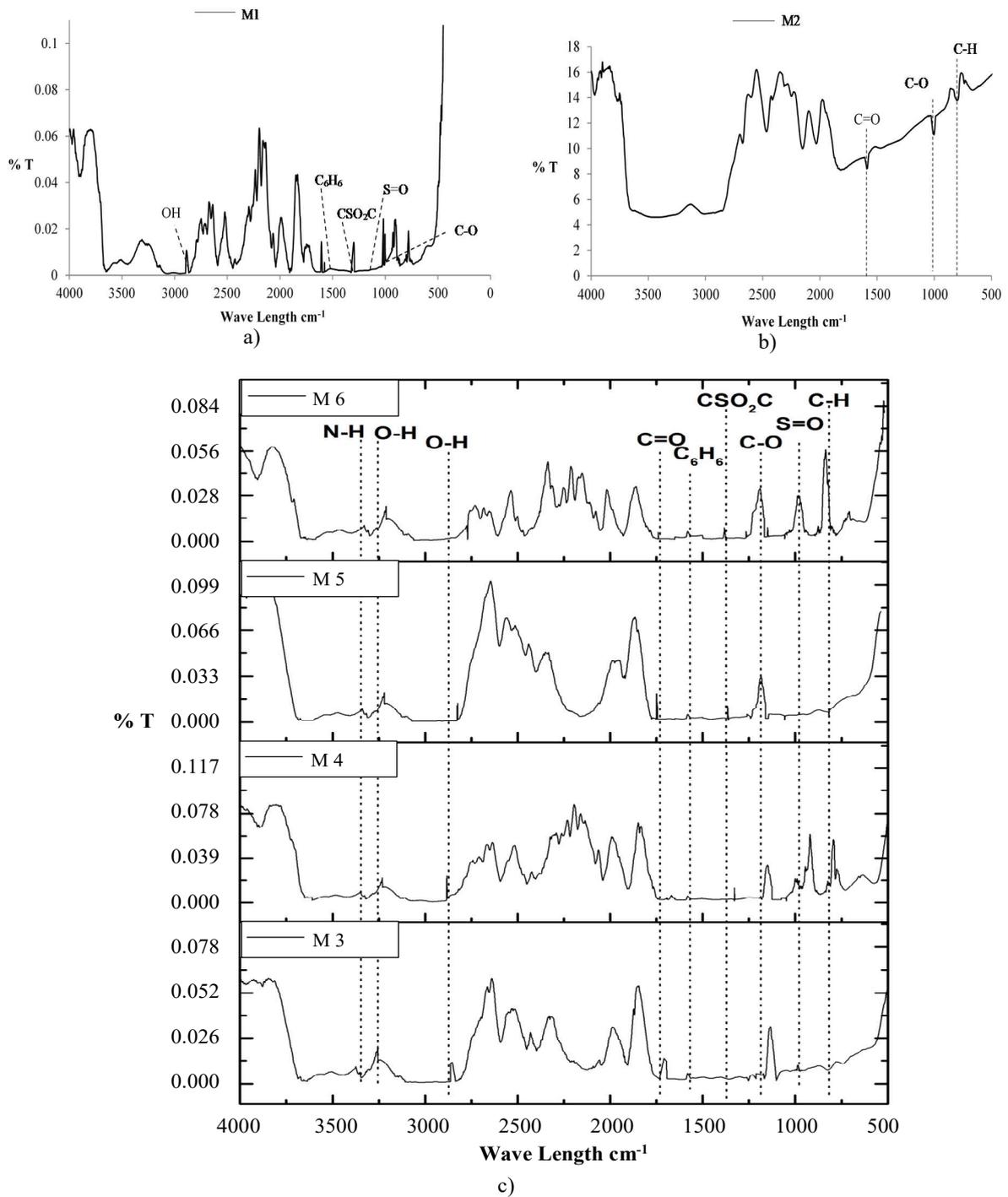
Membrane Sample	Polymer Blend			Degradation MDEA Amine onset temperature (°C)	Maximum MDEA Amine degradation temperature (°C)	Degradation onset PVAc temperature (°C)	Maximum degradation PVAc temperature (°C)	Degradation onset PSU temperature (°C)	Maximum degradation PSU temperature (°C)
	PSU wt/wt%	PVAc wt/wt%	Amine 10%wt/wt						
M1	100	-	-	-	-	-	-	535.13	570.48
M2	-	100	-	-	-	318.54	355.38	-	-
M3	95	5	MDEA	248.42	272.41	360.42	370.60	533.29	566.94
M4	90	10		246.12	270.73	352.44	365.51	530.84	565.33
M5	85	15		245.96	267.25	351.82	364.97	526.61	558.80
M6	80	20		244.15	261.32	345.71	355.87	525.07	557.43

At the end of the degradation, almost 20-25% residual remained. Nevertheless, these results agreed with prior studies [30]. For an effective separation, the polymer should have good interaction in the blend and the important factors, which affect the properties and performance of the membrane are prearrangement of chemical groups attached to the main chain are also some of molecular structure and specific nature. In comparison, alkanol amines decompose at a lower temperature than PSU/PVAc because of the substitution of  $\text{NH}^+$  group.

### Spectral Analysis of Enhanced Polymeric Blend Membrane

Figure 7 (a) shows the FTIR for based PSU membrane with the functional group  $\text{S}=\text{O}$ ,  $\text{CSO}_2\text{C}$ ,  $\text{C}-\text{O}$ ,  $\text{C}_6\text{H}_6$  and the OH aliphatic and aromatic stretch. In based PSU membrane, the  $\text{S}=\text{O}$  sulfone group was symmetric for the PSU wave length, ( $1150.00\text{-}1100.00\text{cm}^{-1}$ ); give the characteristic peak at  $1125.89\text{cm}^{-1}$  without any substantial change caused by vibration stretching. The  $\text{CSO}_2\text{C}$  asymmetric stretch peak seems at  $1323.53\text{cm}^{-1}$  due to hydrogen-bond-accepting groups with repeating unit at the ortho position [31]. The  $\text{C}-\text{O}$  asymmetric stretch peak in PSU ( $1260\text{-}1000\text{cm}^{-1}$ ) shifted to  $1018.45\text{cm}^{-1}$  attributable to hydrogen shift bonding, and the region is associated with the benzene ring stretching mode [32]. The  $\text{C}_6\text{H}_6$  ring stretch (wave number  $1587.00\text{-}1489.00\text{cm}^{-1}$ ) peaked at  $1579.33\text{cm}^{-1}$  as a slight change but otherwise endured stable. The OH aliphatic stretch (wave number  $2886.00\text{cm}^{-1}$ ) band arisen at  $2880.15\text{cm}^{-1}$  because of the weak electro-negativity of the  $\text{OH}^-$  ion. The delocalization of the structure is accountable for the stability of its mechanical properties and its good strength values against oxidative degradation although at high temperatures. Due to the existence of aromatic rings in polysulfone polymer is susceptible to a sulfonation reaction,  $-\text{SO}_3\text{H}$  associations incorporate into their structure [31].

Figure 7 (b) shows the FTIR for based PVAc membrane. This figure represent the functional group that are  $\text{C}-\text{O}$ ,  $\text{C}-\text{H}$  and  $\text{C}=\text{O}$ . The wavelength of  $\text{C}=\text{O}$  is  $1760\text{cm}^{-1}$  to  $1600\text{cm}^{-1}$ , the peak seems on  $1630.65\text{cm}^{-1}$ . The carboxylic group  $\text{C}-\text{O}$ , a peak appears at  $1025.72\text{cm}^{-1}$  due to interactions between hydrogen bonding [33, 34]. The  $\text{C}-\text{H}$  group in phenyl ring substitution bands wavelength is ( $870.00\text{-}675.00\text{cm}^{-1}$ ), the band appears on  $801.85\text{cm}^{-1}$  caused by symmetric stretching in  $\text{CH}_3$  [22, 23]. This band is due to the vibration of symmetric angular deformation outside the  $\text{C}-\text{H}$  plan complex.



**Figure 7.** FTIR of spectral analysis a) based PSU membrane, b) Based PVAc membrane, c) Comparative FTIR spectra of the polymeric blend membranes with MDEA

Figure 7 (c) indicates the addition of 10wt. % MDEA in PSU/PVAc blend of different compositions all previous functional groups (S=O, CSO<sub>2</sub>C, C-O, C<sub>6</sub>H<sub>6</sub>, C-H and C=O) were present in the original position. The new peak C-N appears 1207.21-1241.65cm<sup>-1</sup> for M3 to M6. New absorption bands observed in M3 to M6 membranes in the region of 3374.21cm<sup>-1</sup> - 3378.29cm<sup>-1</sup> are because of N-H stretch band of MDEA. The absorption bands at 3240.93-

3270.11 $\text{cm}^{-1}$  (M3 to M6) are attributed to O-H group of MDEA. The change in wavenumber can be described by the formation of hydrogen bonds among -OH of methyl diethanolamine (MDEA) and oxygen atoms of the sulfone group [31]. It has observed that all the synthesized membranes have the same spectrum, showed that there was no chemical interaction among PSU/PVAc and MDEA hydrogen interactions.

Interestingly, on account of blends with at least some level of compatibility, the shifts of certain significant bands to other frequencies point toward the presence of specific interactions happening among the characteristic groups of the base PSU/PVAc polymers and MDEA. The summarised form of different shifts in the FTIR spectra are presented in Table 3 and supports the development of the interactions among the polymers which indicates their miscibility in the form of blended membranes [22, 23, 35, 36]. The limited degree of peak shifting revealed by FTIR studies confirmed the miscibility of the tested polymer blends.

**Table 3.** Summary of the FTIR spectral of enhanced polymeric blend membranes [22, 23, 35-37]

Polymer	Spectral Assignment	Wave Number $\text{cm}^{-1}$	Based membranes Observed wave number $\text{cm}^{-1}$	PSU/PVAc/MDEA blend membranes Observed wave number $\text{cm}^{-1}$
PSU	S=O symmetric stretch (Sulfone)	1150-1100	1125.89	1105.35-1130.74
	CSO <sub>2</sub> C (Dimethyl sulfone)	1322, 1370-1250	1323.53	1307.28-1324.63
	C-O asymmetric stretch (Carboxylic)	1244, 1260-1000	1018.45	1039.92-1052.54
	C <sub>6</sub> H <sub>6</sub> ring stretch (Benzene)	1587-1489	1579.33	1542.67-1569.39
	OH aromatic and aliphatic stretch	2971, 2938 and 2886	2880.15	2871.72-2889.44
PVAc	C=O stretch (Ketone)	1736,1760-1600	1630.65	1734.66-1744.27
	C-O asymmetric stretch	1244,1260-1000	1025.72	1039.92-1052.54
	C-H phenyl ring substitution band	870-675, 850	801.85	819.83-867.81
MDEA	C-N stretch	1340-1020	-	1207.21-1241.65
	N-H stretch	3500-3300	-	3374.21-3378.29
	O-H stretch	3640-3160	-	3240.93-3270.11

Moreover, there was no formation of intermediates or cross-linking and the frequency shifts observed were peaks that characterised diaryl sulfone, C-O, C=O and N-H groups of PSU/PVAc/MDEA [31]. In these spectral variations point to molecular interactions between the polymer components in the blends, highlighting their compatibility [22, 36, 38]. These observations are in good agreement with previous studies [39-44].

## CONCLUSION

Enhanced Polymeric Blend membrane has been successfully established. The cross sections of blended membranes showed packed bed of spheres that were highly packed. The cross sections also showed good interaction amongst PSU, PVAc polymers with MDEA amine. The kinetic analysis performed on the developed membranes revealed that the thermal degradation temperature decrease with the increase the PVAc contents in PSU. FTIR analysis confirmed miscibility as few shifts in spectra were observed. Moreover, no evidence of cross-linking or intermediate species formations was observed. This enhancement in the properties has been achieved due to the addition of MDEA amine in PSU/PVAc blend membranes. Future studies to replace the MDEA amine by di-iso propyl amines (DIPA).

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## NOMENCLATURE

DMAc	Dimethyl acetamide
DEA	Diethanolamine
EPBM	Enhanced Polymeric Blend Membranes
GPU	Gas permeation unit
MEA	Monoethanolamine
PSU	Polysulfone
PVAc	Polyvinyl acetate
$T_g$	Glass transition temperature

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