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Research Article

Advanced Development and Characterization of DEA Amine-Polysulfone/Polyvinylacetate Blend Membranes

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Abstract: Membrane technology effectively separates CO_2 from CH_4 and has been practiced for many years but requires membranes with high selectivity and permeability. Different approaches are employed to improve membrane performance and it is soon possible to develop a blended polymeric membrane that separates high pressure gas streams at the point of processing pressure. However, glassy polymers suffer a lack of permeability causing their performance to drop as an upper bound trade-off but highly selective and rubbery polymers have high permeability with low selectivity. As an amine solution is capable of purifying naturally acidic gas, blending glassy, rubbery polymers with amines-specifically, polysulfone and polyvinyl acetate with diethanol amine in dimethyl acetamide as solvent-we developed flat sheet membranes with desirable properties. As it is now possible to acquire amine-polymer blends with more desirable properties by mixing with a miscible polymer, it is essential to observe factors that affect the polymer's miscibility with amines. Hence, we also analyzed the effects of blend ratios on different properties. Blended membranes of different ratios were synthesized and their functional groups were characterized by Fourier Transformed Infra-Red spectroscopy (FTIR). We then employed Thermal Gravimetric Analysis (TGA) to describe weight loss and Field Emission Scanning Electron Microscopy (FESEM) to determine respective morphologies.

Keywords: Blending, diethanol amine, dimethylacetamide, polysulfone, polyvinyl acetate

INTRODUCTION

Various CO_2 capture technologies exist for the removal of CO_2 from natural gas. These include physical absorption (Littel *et al*., 1990; Chiesa and Consonni, 1999); chemical absorption (Bishnoi and Rochelle, 2002; Aroonwilas and Veawab, 2004; Rochelle, 2009); adsorption (Harlick and Tezel, 2004; Cheng and Tan, 2009); and membrane (Powell and Qiao, 2006). Membrane technology is a valued method for the separation of CO_2 from CH_4 and has been in use for many years. It holds numerous advantages over other techniques that are more appropriate for gas separation in certain sectors (Wee *et al*., 2008; Wind *et al*., 2004; Baker, 2004; Ismail and David, 2001; Sanders, 1988). For this reason and since membranes with high selectivity and high permeability are increasingly desired, procedural enhancements of polymeric membranes have been explored that include the development of mixed matrix membranes (Hussain, 2006; Vu *et al*., 2003; Moore, 2004; Chung *et al*., 2007); polymer blend membranes (Acharya *et al*., 2008; Semsarzadeh and Ghalei, 2012; Hosseini *et al*., 2008; Khan *et al*., 2011) that include a carbon dioxide solvent such as ionic liquids within the polymer matrix to increase carbon dioxide solubility (Bara *et al*., 2007; Oral *et al*., 2011; Tang *et al*., 2005).

Polymeric membranes have different performance mechanisms that are based on physical and chemical structural properties that govern interactions between the membrane's components and gases. Polymeric membranes are also classified according their polymer materials. Glassy polymers are rigid, glass like structures that operate below the glass transition Temperature (Tg) and are highly selective but have low permeability; of such is Polysulfone (PSU) which has a high Tg. Many researchers are attracted to PSU and seek to increase both its permeability and selectivity (Ghosh and Banerjee, 2008; Mehdipour-Ataei and Amirshaghaghi, 2005; Zhang *et al*., 1999). Rubbery polymers are soft and elastic and operate above Tg. They have low selectivity but high permeability; of such is polyvinyl acetate.

Amines with two hydrogen atoms directly attached to a nitrogen atom, such as Monoethanolamine (MEA) and 2- (2-aminoethoxy) ethanol (DGA), are called primary amines and are generally the most alkaline. Diethanolamine (DEA) and Diisopropanolamine (DIPA) have one hydrogen atom directly attached to the nitrogen atom and are called secondary amines. Triethanolamine (TEA) and Methyldiethanolamine

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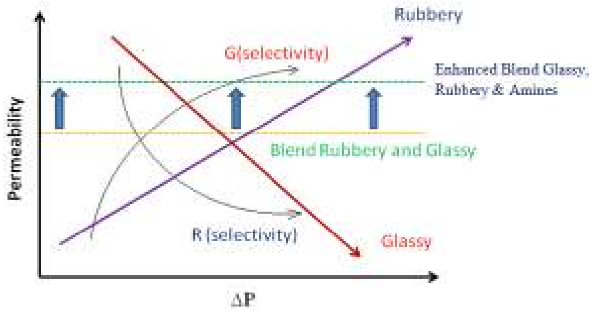


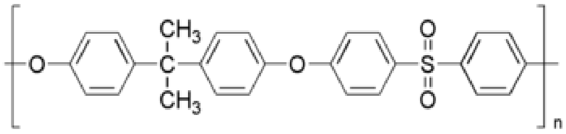
Fig. 1: Current trend of enhanced polymeric blend membrane (Mushtaq *et al*., 2013)

(MDEA) represent completely substituted ammonia molecules without hydrogen atoms attached to the nitrogen and are called tertiary amines. Amine solutions therefore have the potential to purify acidic natural gas (Kerry, 2007). Hence, the blending of both glassy and rubbery polymers with DEA amines solutions for the purpose of enhancing the ability to separate CO_2/CH_4 mixtures is the current trend as shown in Fig. 1. As amines naturally attract both CO_2 and H_2S, they allow for a well-organized and valuable removal function as a desired performance characteristic for suitably blended polymeric membranes in the search for higher selectivity and permeability.

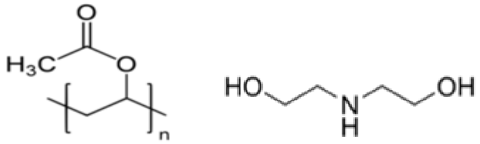
Hence, this study examined PSU/PVAc/DEA, prepared as dense, flat sheet blended polymer membranes with different polymer blended ratios to study effects on morphology, polymer-polymer interactions with amines, as well as thermal stability. These blended membranes were characterized by FESEM, FTIR and TGA for comparison with individual polymers.

METHODOLOGY

Materials and membrane fabrication: Polysulfone (PSU) (Udel® P-1800) with a glass transition Temperature (T_g) of 185°C was acquired from Solvay Advanced Polymers. L.L.C. (U.S.) PSU was provided in a minced form. Polyvinyl Acetate beads (PVAc) (average M_w ~100,000 by GPC) were obtained from Sigma Aldrich with a T_g of 30°C. Diethanol amine and Dimethyl Acetamide (DMAc) solvent (99.99% pure) was purchased from Merck.



(a) Polysulfone



(b) Polyvinyl acetate (c) Diethanol amine

Fig. 2: Structure of polysulfone, polyvinyl acetate and diethanol amine

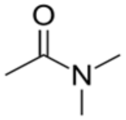


Fig. 3: Structure of Dimethylacet Amide (DMAc.)

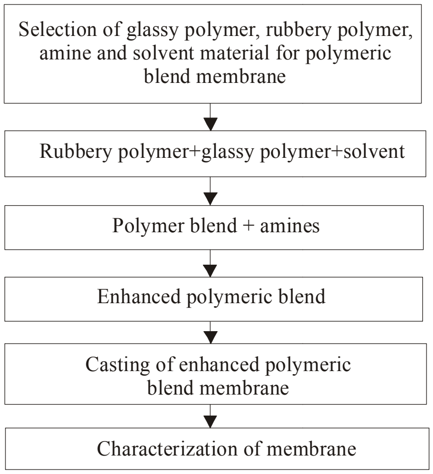


Fig. 4: Research methodology

Table 1: Composition of different polymer blend membranes

Blending 20% W/W	Solvent DMAc. 80% (%)	Polymer 20% PSU (%)	PVAc. (%)	Amine DEA (%)
	100	100	0	-
		0	100	
	90	100	-	10
		95	5	
		90	10	
		85	15	
		80	20	

The blending of polysulfone and polyvinyl acetate with Diethanol amine (Fig. 2) was done using Dimethylacetamide (DMAc) as solvent (Fig. 3) at a ratio of 20% wt/wt with 80% without amine and 20% polymer equaling total weight. PSU was pre-heated for one night to remove moisture content. Initially, PVAc was allowed to completely dissolve in the DMAc solvent after which the glassy polymer and amine were added and continually stirred for 24 h at room temperature to obtain an homogeneous mixture. This was followed by bath sonication in Transonic Digital S, Elma® for one hour for the purpose of degassing and to achieve a clear solution. Both polymers were completely dissolved in solvent and there was no sign of agglomeration or settling on standing. Thus we can say they were miscible. This doped solution was then cast on a glass plate with a casting knife having an opening of 200 µm. The casted membrane was then placed at room temperature for 5 days to evaporate all solvent after which they were peeled from glass plate for characterization. Different compositions of our polymeric blended membranes are shown in Table 1 and our methodology is clearly defined in Fig. 4.

Characterization: The synthesized membranes were characterized according to effects derived from the polymer blending on syllable structure, chemical interaction and thermal stability. Amine polymeric membranes were characterized by, Field Emission Scanning Electron Microscopy (FESEM) (SUPRA 55VP by ZEISS) was used to observe resultant morphology using surface and cross sectional images after all membrane samples were dipped in liquid nitrogen and fractured. The surface view magnification was 500X. The FTIR scan result (Perkin Elmer Spectrum One FTIR Spectrometer) was 20 with a wave length range of 4000-450 cm^{-1} with spectra obtained from a 200 µm diameter sampling area. All membrane samples were cut from randomly selected positions from the casting films and clamped to the plate. All spectra were corrected for FTIR's characteristic progressive increases in absorbance at lower wave numbers using the equipment's software. Thermogravimetric Analysis (TGA) determined thermal stability at temperatures ranging from 28-800°C while heating at 10°C/min.

RESULTS AND DISCUSSION

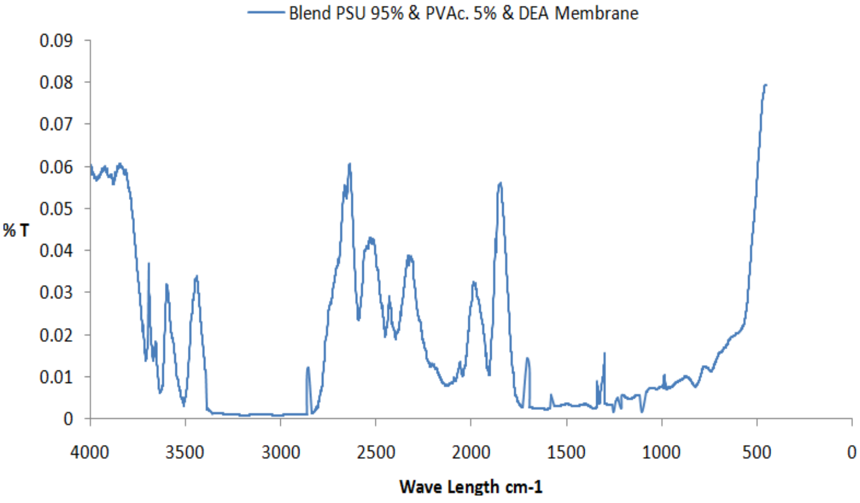
FTIR: A complete frequency analysis of FTIR spectra for PVAc, PSU and DEA were recorded. Chemical structures are shown in Fig. 2 and 3 and spectra are shown Table 2. A discussion of these results now follows.

As the Figure indicates (1a, 1b, 1c, 1d), the sulfone group (S = O) was symmetric for polysulfone (wave number 1150.00 cm^{-1}) with peaks shifted to 1103.17, 1150.11, 1000.73 and 1095.23 cm^{-1}, respectively; no large changes were noted due to vibrational stretching. The CSO$_2$C asymmetric stretch was slightly shifted to peaks at 1253.39, 1310.26, 1306.41 and 1320.16 cm^{-1}, respectively due to hydrogen bonding. The C-O symmetric stretch for PSU and PVAc (1244 cm^{-1}) showed peak shifting to 1228.83, 1060.54, 1170.59 and 975.78 cm^{-1}, respectively also due to hydrogen bonding (Ahmed *et al.*, 2011). The ring stretch for C$_6$H$_6$ (1587.00 cm^{-1}) peaked at 1580.26, 1580.67, 1566.80 and 1587.27 cm^{-1}, respectively with slight changes yet remained stable overall. The OH Aliphatic stretch peaks (2886.00 cm^{-1}) occurred at 2853.88, 2860.44, 2815.93 and 2795.42 cm^{-1}, respectively due to the weak electro-negativity of the OH negative ion.

Figure 5a to d of the C = O ketone in PVAc showed peaks shifted to 1732.82, 1730.3, 1709.62

Table 2: FTIR Spectra of PSU, PVAc and DEA

	Wave number/cm									
Spectra	S = O symmetric stretch	CSO$_2$C asymmetric stretch	C-O asymmetric stretch	C$_6$H$_6$ ring stretch	OH aliphatic and aromatic stretch	C = O	C-H	C-N stretch	O-H stretch	N-H stretch
PSU	1150, 1307	1322	1244	1587-1489	2886, 2938 and 2971	-	-	-	-	-
PVAc.	-	-	1244, 1260-1000	-	-	1736, 1760-1670	850, 870-675	-	-	-
DEA	-	-	-	-	-	-	-	1020-1340	3160-3640	3300-3500



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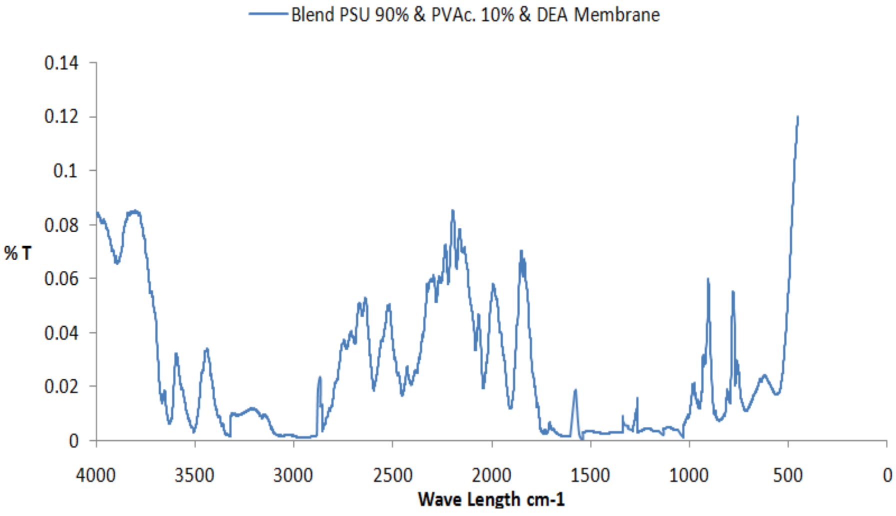

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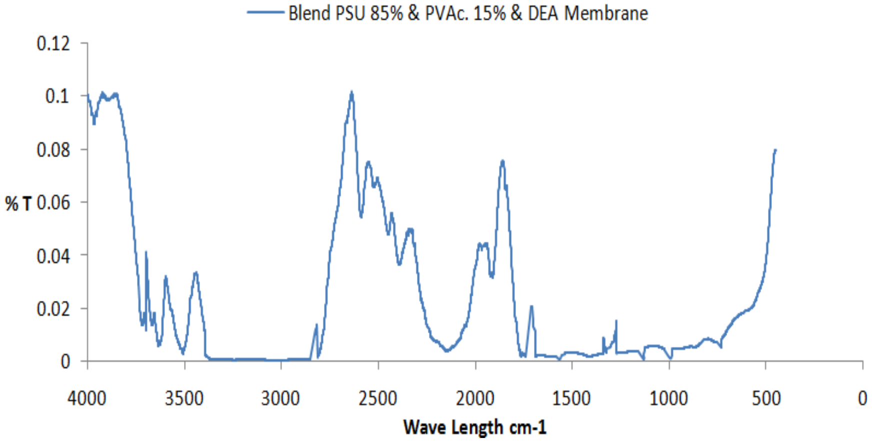

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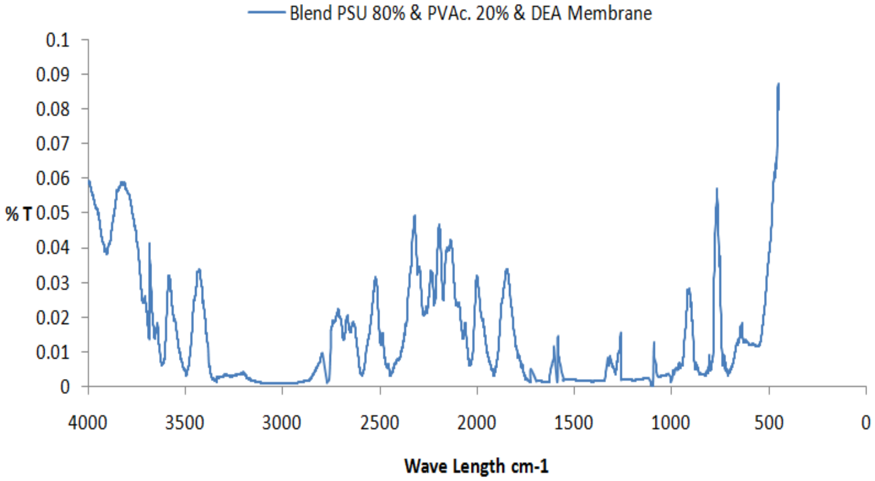


(d)

Fig. 5: FTIR graph of (a) polymer 20% (PSU 95%/PVAc. 5%) and DEA 10% (b) polymer 20% (PSU 90% /PVAc. 10%) and DEA 10% (c) polymer 20% (PSU 85%/PVAc. 15%) and DEA 10% (d) polymer 20% (PSU 80%/PVAc. 20%) and DEA 10%

and 1725.46 cm^{-1}, respectively without change in structure bonding but slight vibrational variance due to stretching and/or the amide group. The C-H Phenyl ring substitution (850 cm^{-1}) peak shifted towards 846.35, 842.23, 753.17 and 857.39 cm^{-1}, respectively; slightly changed from its original position but within range due to its stable hydrogen bonding and/or asymmetric stretching of CH_3 (Morris, 1943; Jensen *et al*., 1972).

Figure 5a to d show the amine group (C-N) at 1280.03, 1282.24, 1266.29 and 1283.19 cm^{-1}, respectively due to the replacement of hydrogen bonding. The OH amine group band appears at 3625.08, 3619.62, 3617.77 and 3608.18 cm^{-1}, respectively due to the electro-negativity of its hydroxyl group. The N-H group's peaks in Fig. 5a to d occur at 3499.93, 3494.62, 3495.27 and 3488.67 cm^{-1}, respectively due to vibrations that reflect the hydrogen bonding of amide groups (Siesler and Holland-Moritz, 1980) where hydrogen bond formation generally shifts to a lower frequency due to the N-H. This is an important piece of data as hydrogen bonding is a strong intermolecular interface that affects miscibility.

From our FTIR analysis combined in Fig. 6, we posited that the miscibility of the polymeric blends was confirmed by the cited shifts in the spectra and that neither cross linking nor the formation of intermediates occurred. FTIR analysis showed frequency shifts that identified characteristic peaks of di-aryl sulfone, C = O

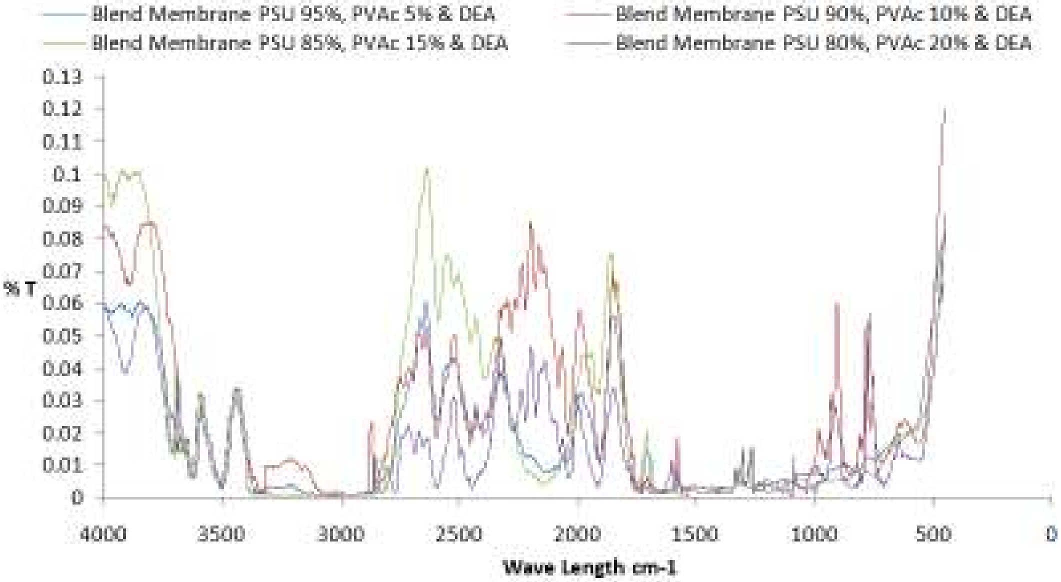


Fig. 6: Combined FTIR graph of (a) polymer 20% (PSU 95%/PVAc. 5%) and DEA 10% (b) polymer 20% (PSU 90% /PVAc. 10%) and DEA 10% (c) polymer 20% (PSU 85%/PVAc. 15%) and DEA 10% (d) polymer 20% (PSU 80%/PVAc. 20%) and DEA 10%

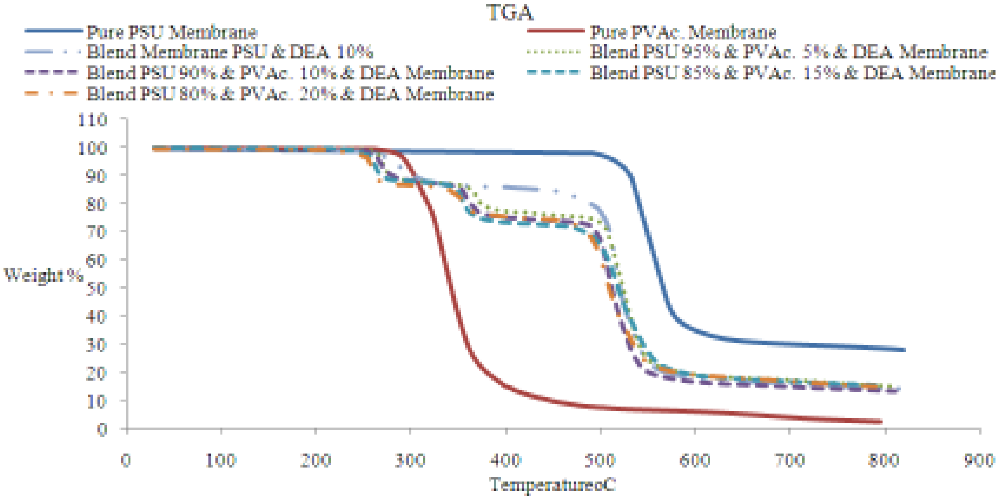


Fig. 7: TGA graph of developed polymeric amine blend membranes

and C-O groups of PSU/PVAc. These spectral changes indicated the existence of molecular interactions within the experimental polymeric blends which endorsed compatibility.

Hydrogen bonding perturbs NH and OH groups by changing the electronic environment which then provides the enthalpy that favors mixing. Enthalpy from hydrogen bond formation is always negative when a self-associating polymer molecule is a component of a mixture. The positive contribution to any change in enthalpy arises from the breaking of the hydrogen bonds within self-associating molecules (Siesler and Holland-Moritz, 1980).

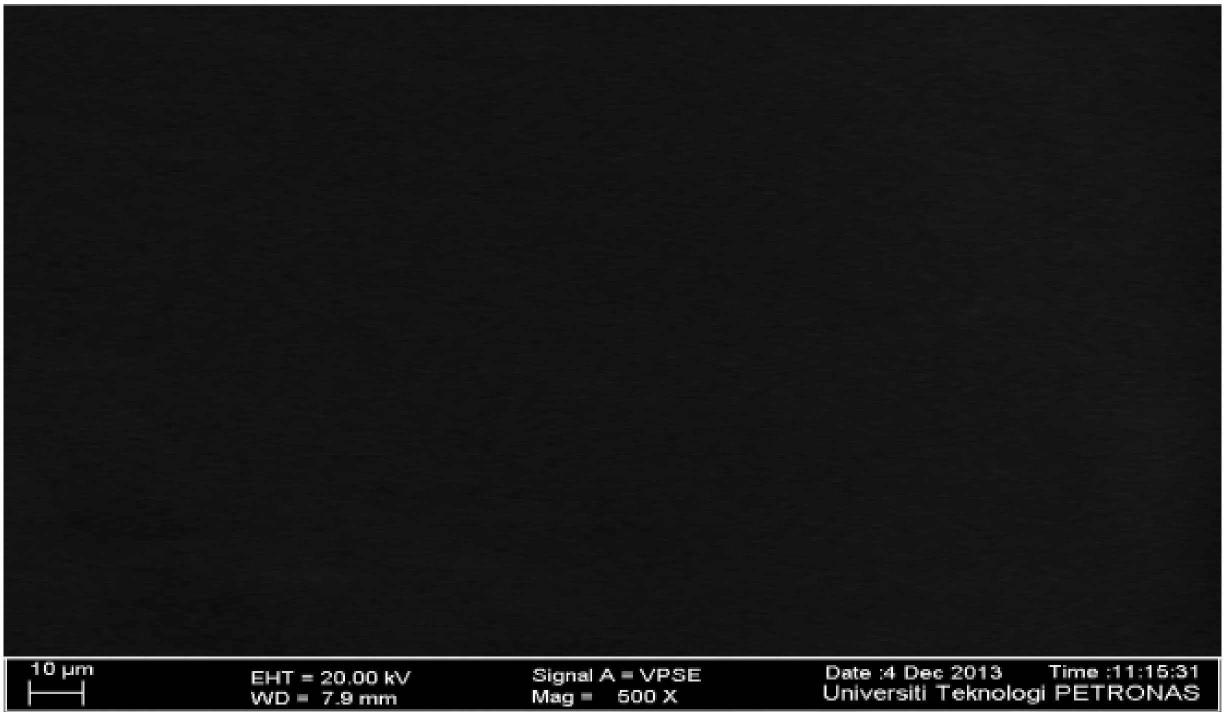
TGA: The thermal degradation temperature of the experimental polymeric blended membranes was analyzed by Thermal Gravimetric Analysis (Fig. 7). Pure PSU, pure PVAc, as well as DEA blended with PSU and PVAc polymer membranes were synthesized in DMAc solvent. The PSU polymer membrane began its degradation at 535.13°C and continued until 570.38°C. The PVAc polymer membrane began degrading at 318.54°C and reached a maximum degradation temperature of 355.38°C.

The DEA blended membranes showed degradation behavior between that of the pure PSU and PVAc polymers. The addition of DEA to PSU and PVAc polymer matrices appears to have altered the thermal stability. With PSU at 95% and PVAc at 5% with 10% DEA amine, the stability of the resultant blend changed from 514.95 to 541.97°C of PSU; from 366.51 to 375.17°C of PVAc and from 265.94 to 280.49°C of 10% DEA amine. Whereas with a blend of PSU (90%), PVAc (10%) and DEA amine (10%), the onset of thermal degradation began at 509.82, 354.64 and 262.31°C, respectively, while end temperature degradation decreased to 535.62, 369.29 and 275.78°C, respectively. For the blended membrane PSU

Table 3: Thermal degradation temperature of polymeric blend membrane

	Polymer blend								
Membrane sample	PSU (%)	PVAc. (%)	Amine 10%	Degradation DEA amine onset temperature (°C)	Max. DEA amine degradation temperature (°C)	Degradation onset PVAc. temperature (°C)	Max. degradation PVAc. temperature (°C)	Degradation onset PSU temperature (°C)	Max. degradation PSU temperature (°C)
1	100	0	-	-	-	-	-	535.13	570.38
2	0	100	-	-	-	318.54	355.38	-	-
3	95	5	DEA	265.94	280.49	366.51	375.17	514.95	541.97
4	90	10		262.31	275.78	354.64	369.29	509.82	535.62
5	85	15		257.62	269.17	349.86	366.05	505.39	530.52
6	80	20		254.28	265.57	345.78	360.18	501.35	521.69

Max.: Maximum



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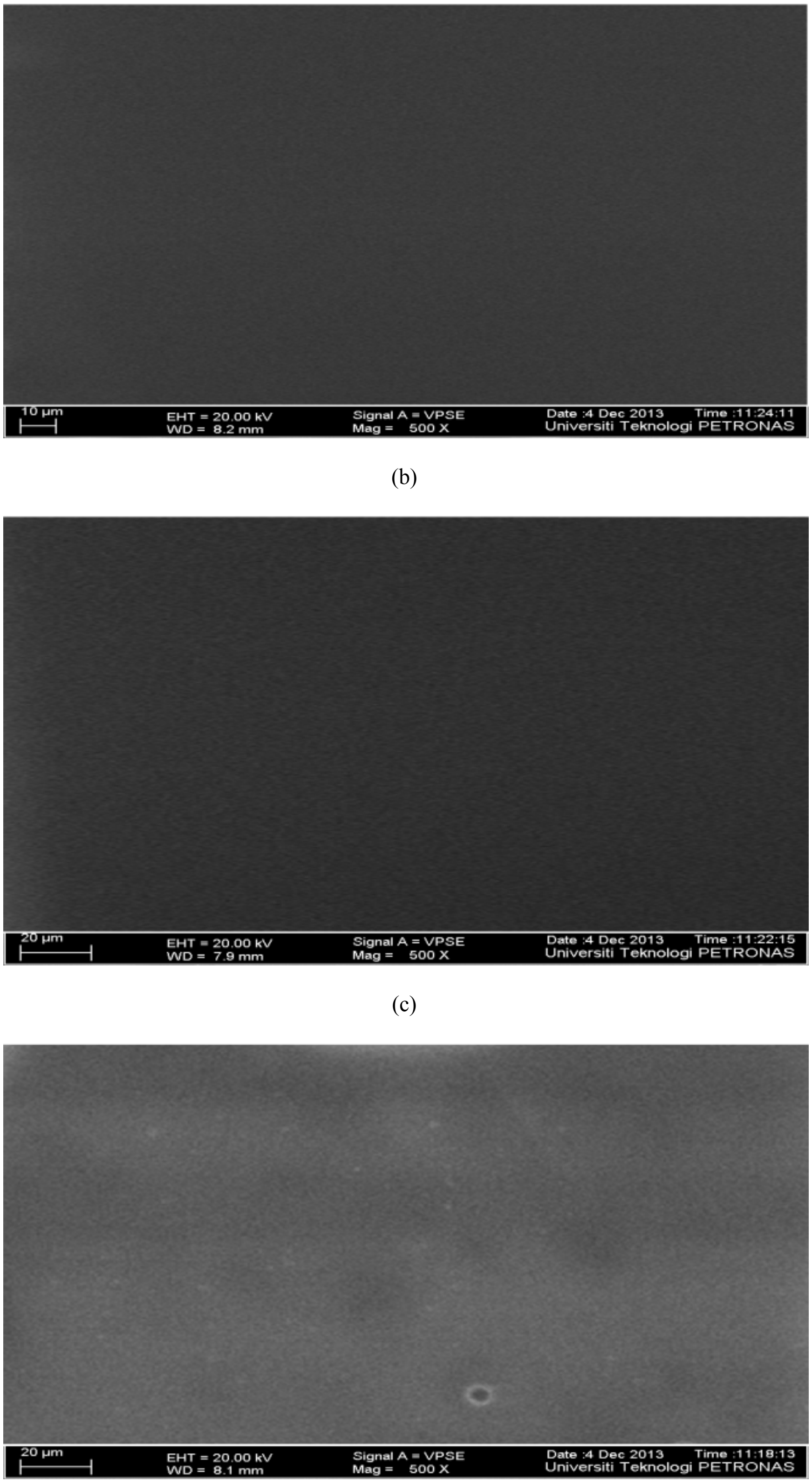


(b)

(c)

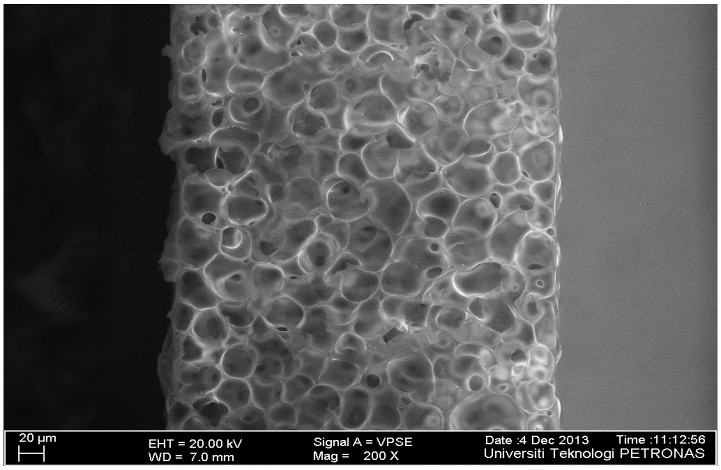
(d)

Fig. 8: Membrane surface view of (a) polymer 20% (PSU 95%/PVAc. 5%) and DEA 10% (b) polymer 20% (PSU 90% /PVAc. 10%) and DEA 10% (c) polymer 20% (PSU 85%/PVAc. 15%) & DEA 10% (d) polymer 20% (PSU 80%/PVAc. 20%) and DEA 10%

(85%), PVAc (15%) with DEA amine at (10%), degradation temperature onset was reduced to 505.39, 349.86 and 257.62°C, respectively, with maximum degradation temperature rises of 530.52, 366.05 and 269.17°C, respectively. Similarly, this cited trend was also shown with blends of PSU (80%), PVAc (20%) and DEA (10%) with degradation onsets at 501.35, 345.78 and 254.28°C, respectively, and maximum degradation temperatures of 521.69, 360.18, and 265.57°C, respectively. The addition of amine caused a change (decreased degradation temperatures) in thermal behavior from what was expected. Such behavior requires further study of thermal degradation kinetics. Nevertheless, these results agreed with prior studies (Rafiq *et al*., 2012). Table 3 summarizes our Thermal Degradation results.

FESEM: Different compositions of PSU, PVAc and DEA amine flat sheet dense blended membranes were synthesized via solution casting and evaporation as described above. FESEM images of these membranes are presented in Fig. 8 through 9. Different compositions of PSU, PVAc and DEA amine blended membrane morphology were compared. Polymer surfaces are represented as follows: Figure 8a presents Polymer 20% (PSU 95%/PVAc 5%) and DEA (10%); Fig. 8b presents Polymer 20% (PSU 90% /PVAc 10%) and DEA 10%; Fig. 8c presents Polymer 20% (PSU 85%/PVAc 15%) and DEA (10%); Fig. 8d presents Polymer 20% (PSU 80%/PVAc 20%) and DEA (10%). It is clear from these figures that dense membranes were effectively synthesized without pores or polymer agglomeration. Their surfaces were also uniform and without signs of phase separation which further confirmed the miscibility of PSU and PVAc polymers with DEA amine (Houde *et al*., 2012).

Similarly, on comparing cross sections: Figure 9a presents Polymer 20% (PSU 95%/PVAc 5%) and DEA (10%); Fig. 9b presents Polymer 20% (PSU 90% /PVAc 10%) and DEA (10%); Fig. 9c presents Polymer 20% (PSU 85%/PVAc 15%) and DEA (10%); Fig. 9d presents Polymer 20% (PSU 80%/PVAc 20%) and DEA (10%). The blended membranes were highly packed with a uniform pore structure. These cross sections indicated good interaction between PSU and PVAc polymers with DEA amine.



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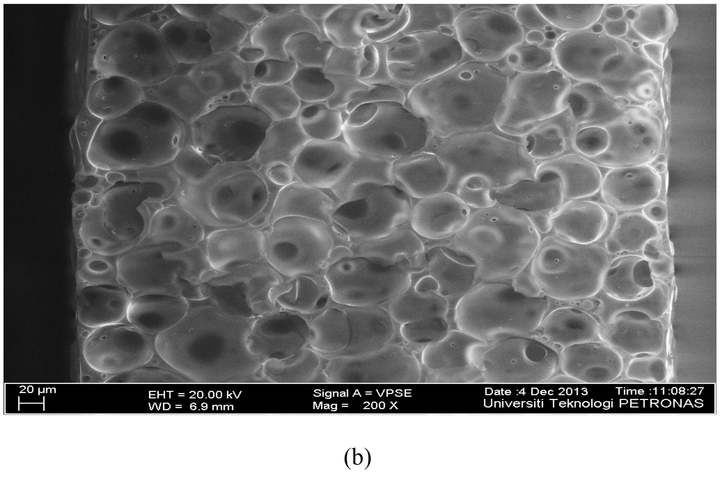

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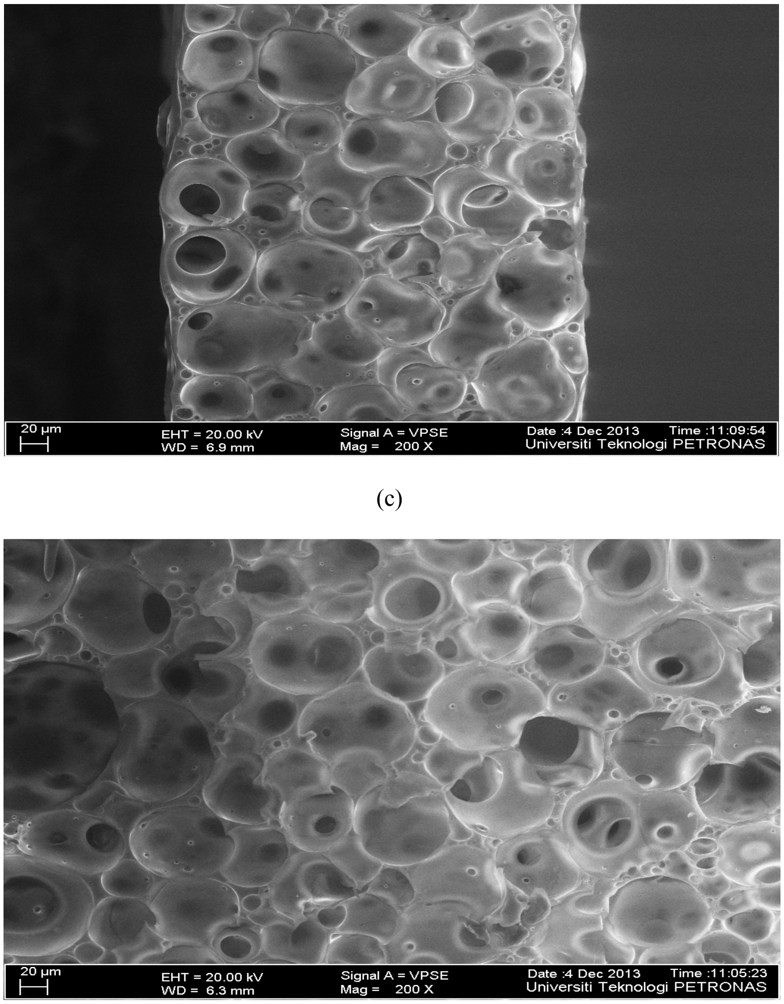

(c)

(d)

Fig. 9: Membrane cross section view of (a) polymer 20% (PSU 95%/PVAc. 5%) and DEA 10% (b) polymer 20% (PSU 90% /PVAc. 10%) and DEA 10% (c) polymer 20% (PSU 85%/PVAc. 15%) and DEA 10% (d) polymer 20% (PSU 80%/PVAc. 20%) & DEA 10%

CONCLUSION

Polymeric Amine Blended Membranes provide an advanced technological solution for gas separation. The blending of environmentally friendly polysulfone and polyvinyl acetate with diethanol amine is a suitable tool for the production of novel materials with combined characteristics that promise improved application properties with low cost advantages in material performance. The surface and cross sectional views of PSU, PVAc with DEA amine indicated excellent interactions between molecules that confirmed the polymer's miscibility. FTIR results also demonstrated favorable intermolecular hydrogen bonding that freed energy for mixing. Also, the addition of diethanol amine to PSU and PVAc polymers affected changes in thermal behaviour from the expected so that degradation temperatures fell. In the future we suggest adding inorganic fillers such as carbon molecular sieves and zeolites to the blend to further enhance the membrane. We fully expect this will prove economically feasible and advantageous for the gas industry.

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