Blending Behavior of Polymeric Materials and Amines in Different Solvents

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***Abstract*—In this paper, research has been carried out to identify the blending behavior of glassy and rubbery polymers in solvent with amines. A strategy to introduce new products into the market without a large investment is to take different polymers, amines and blend them together to make a new product with distinctive properties. The blending of polysulfone, polyethersulfone, polyvinyl acetate and methyl diethanol amine, mono ethanol amine, diethanol amine are examine with dimethyl acetamide and normal methyl pyrrolidinone solvents, which gives the results of appearance, viscosity and pH values by using viscometer and general pH testing method. By getting these results, the miscibility of the mixture was finally established which shows that the heterogeneous or homogenous blends are depending on the blend preparation method. The success of this approach has been limited, as the mechanical properties of the blend with amines are classically worse than a simple mixing law would predict.**

***Index Terms*—Blending, glassy polymer, rubbery polymer, solvents, amines.**

I. Introduction

Polymer blending with amines is considered as time and cost effective method to develop materials with desirable properties. Polymer Blend (PB) is a mixture of two polymers or copolymers. Polymer blends are now more important in particular sectors of polymer industry [1], as they can frequently meet performance requirements that cannot be satisfied by the currently available commodity polymers. Consequently, their attractiveness increases with the increasing demands for this class of materials. As a logical consequence, many studies have been devoted to polymer blends, with special emphasis on their mechanical and thermal behavior. It is possible to obtain polymer blends of more desirable properties by mixing miscible polymers, and thus it is very important to examine the factors affecting the miscibility of polymer mixtures. The miscibility term describes the homogeneity of polymer mixtures at some temperatures.

Previous research found that polymeric membrane having good repute in natural gas purification [1]. In this research study we prepare the polymer blend of polymeric membrane by the combination of glassy and/or rubbery polymer and mixing the amines. This method leads to improve the separation ability for CO_2/CH_4 mixture because polymeric blend membrane using the properties of both glassy and/or rubbery phases with good permeability, selectivity, mechanical strength and chemical stability. As Table I shows different studies regarding on polymer blend membrane. However, blending of glassy and rubbery polymers with amines has not been studied.

The detailed composition of polymers and solvents is given in this Table II. On the basis of these reports, the blending behavior of polymers will be further proceed.

The amine solution has the capability to purify the natural gas having acid gas. Amine has a natural affinity for both Carbon dioxide and Hydrogen Sulphide allowing this to be a very efficient and effective removal process [2]. The following Table III shows the comparison of different amines properties.

II. Background

The separation methods for removing CO_2 can either be bulk or trace removal depending on the application. The principal factors that are usually considered when choosing a suitable separation schemes are product purity, feed and products gas partial pressure needs, operating temperatures, energy needs, and also the presence of impurities within the gas. Fig. 1 shows the approximate ranges of application of different types of gas treating processes for CO_2 removal in the feed gas.

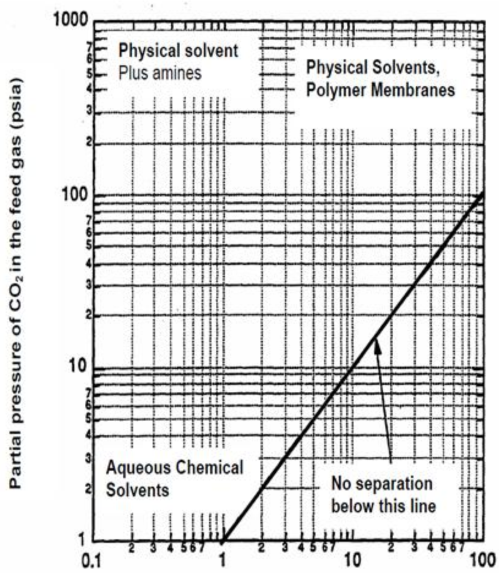

Fig. 1. Partial pressure of CO_2 in the product gas (psia) [3].

Amine-containing chemical solvents are generally preferred when the partial pressure of CO_2 in the feed gas is relatively low or when CO_2 reduced to a very low concentration in the treated gas. Physical solvents are used at high CO_2 pressures in the feed gas and when deep CO_2 removal is not required.

Manuscript received August 1, 2013; revised November 26, 2013. This work was supported by the Universiti Teknologi PETRONAS, Depart-ment of Chemical Engineering. Paper title is Blending Behavior of Polymeric Materials and Amines in different Solvent.

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DOI: 10.7763/IJCEA.2014.V5.365

TABLE I: DIFFERENT STUDIES REGARDING ON BLEND MEMBRANE

Sr. No.	Year	Polymers	System	Remarks	Ref
1	2002	PES/PI (Glassy/Glassy) coated with PDMS	Gas separation	Hollow fiber	[4]
2	2006	PU based PEI/PAI (Glassy/Glassy) blend	CO_2		[5]
3	2006	PU/PDMS (Rubbery/Rubbery) cross-linked	Gas mixture		[6]
4	2006	PVDF/PES (Glassy/Glassy)		studied effect of polymer concentration, solvent & morphology	[7]
5	2009	PVAm/PVA with porous PES support	Facilitated CO_2 transport	Ultra-thin membrane with good strength, stability and permeability/selectivity	[8]
6	2008	PES/PI (Glassy/Glassy) blend MMM	O_2/N_2		[9]
7	2010	PU/PDMS (Rubbery/Rubbery)	methanol/toluene	per vaporization	[10]
8	2010	PEG/PDMS	CO_2 separation		[11]
9	2010	PU/CA(porous) (Glassy/Rubbery)	Micro filtration		[12]
10	2010	PES/PI (Glassy/Glassy)	O_2/N_2		[13]
11	2011	SPEEK/ Matrimid	CO_2 separation	Cross-linked for anti-plasticization	[14]
12	2011	PSF/PI (Glassy/Glassy)	CO_2/CH_4	studied effect of solvents	[15]
13	2011	PEI/PVP	CO_2/CH_4, CO_2/N_2	Carbon hollow fiber membrane	[16]
14	2012	PES (PVP or PEG) with PDMS coating	toulene/water	per vaporization	[17]
15	2012	PU/PVAc with PEO/PPO	Gas mixture	increased CO_2 permeability	[18]
16	2012	PIM-1/ Matrimid	CO_2/CH_4 , CO_2/N_2	increased selectivity	[19]

Abbreviations: CA=cellulose acetate, PAI=polyamide imide, PDMS=polydimethyl siloxane, PEA=aromatic polyether amide, PU=polyurethane, PEG=polyethylene glycol, PEI=polyether imide, PSF=polysulfone, PEO=polyethylene oxide, PES=polyether sulfone, PI=polyimide, PIM-1=polymer of intrinsic micro porosity, PPO=polypropylene oxide, PVA=polyvinyl alcohol, PVAc=polyvinyl acetate, PVAm=polyavinylamine, PVDF=polyvinylidene fluoride, PVP=polyvinyl, SPEEK=sulfonated aromatic poly(ether-ether-ketone)

TABLE II: DIFFERENT STUDIES REGARDING POLYMER BLEND COMPOSITION

Polymer A	Polymer B	Solvent	Blend composition	Ref.
PES (%)	PI (%)	NMP	35% , 30%, 26% in solvent, respectively	[4]
80	20			
50	50			
20	80			
PSU (%)	PI (%)	(NMP/DCM) (%) 80/20,50/50, 20/80	25 g polymer was used.	[15]
100	0			
95	5			
90	10			
85	15			
80	20			
PSU (%)	PVAl (%)	DMF	10 % in solvent	[18]
100	0			
95	5			
90	10			
85	15			
PSU (%)	PI (%)	Methylene chloride (DCM)	5 wt % of solution	[20]

TABLE III: COMPARISON OF DIFFERENT AMINES [21]

Amine / Properties	DEA	DGA	MEA	MDEA	DIPA
Molecular Wt.	105.14	105.14	61.08	141	101.19
B.P (^oC)	221	515.1	171	247	85
Solubility in H_2O	Complete	Complete	Complete	Complete	Slightly Soluble
Color	Colorless	Colorless	White	Colorless	Colorless
Odor	Mild amine odor	Mild ammoniacal odor	Mild ammoniacal odor	Ammoniacal odor	Fishy, Ammonical
Heat of reaction kJ / kg CO_2	1510	1729	1920	1420	2180
Capability of CO_2 in feed stream	5-10%	15-20%	20-25%	20-40%	20-35%
Amine Efficiency Strength wt %	50-70	25-35	15-20	20-50	30-50
Acid Gas loading mole/mole	0.3-0.35	0.3-0.35	0.3-0.35	Unlimited	0.41-0.61

In addition, the discovery and development of new polymers blend has made separation of gases by membranes competitive in relation to the conventional methods of scrubbing using physical or chemical solvents. As within the gas scrubbing processes, the absorption of the reactive gas (*e.g.* CO_2) can be improved by the addition of reactive carrier to the matrix. As a result, further increase in the mass transport can be achieved when the carrier reacts preferentially with a component of the diffusing gases. This phenomenon is referred to as Facilitated Transport.

Several researchers have investigated the chemistry of CO_2-amine solutions over the years due to its important industrial application for the removal of CO_2 from gas streams. The overall reaction between CO_2 and primary or secondary amines is

$$CO_2 + 2R_1R_2NH \rightleftharpoons R_1R_2NH_2^{\ +} + R_1R_2NCO_2$$

where R represents the functional groups (for MEA, $R1$ = -H, $R2$ = -CH_2CH_2OH; for DEA, $R1 = R2$ = -CH_2CH_2OH).

The Dankwerts' zwitterions mechanism has recently become one of the most widely accepted mechanism for primary and secondary amine reaction with CO_2 [22].

From Fig. 2, polymer blending offers time and cost effective method to develop materials with desirable properties. Therefore effect of blending of a glassy and a rubbery polymer with different amines solutions, for that purpose to improve the separation ability for CO_2/CH_4 mixture. The amine solution has the capability to purify the natural gas having acid gas. Amine has a natural affinity for both CO_2 and H_2S allowing this to be a very efficient and effective removal process. and also with topping of amines on the performance of polymeric membrane should be research so that a membrane with high selectivity and high permeability could be developed.

Materials for Gas Separation Membrane

The selection of material membrane is the most important factor for Gas Separation. Chemical interaction between a membrane material and a gas penetrate determined the separation efficiency of a membrane separation process [23].

The choice of material is based on the application and cost-effectiveness. The most important requirements of effective separation material are: [24], [25]

- Engineering feasibility.
- Good chemical resistance.
- High separation efficiency with reasonable high flux.
- Good mechanical stability.
- High thermal stability.
- Low cost.

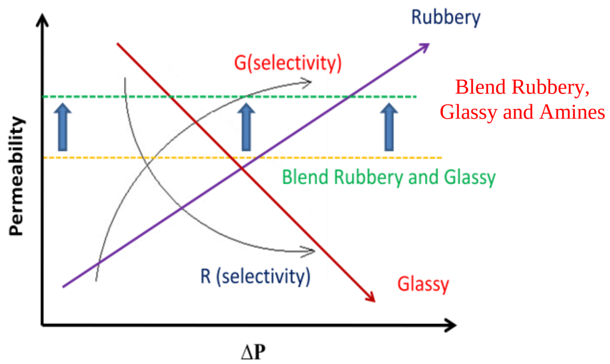


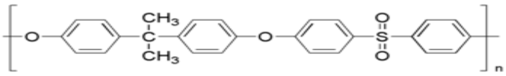
Fig. 2. Current Trend of Polymeric Blend Membrane.

III. METHODOLOGY

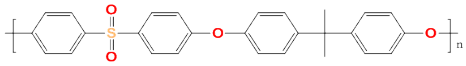
In this study, the main objective is to develop a "Polymer Blend" which is the combination of Glassy, Rubbery Polymer and amine with solvent. For the developed of polymeric blend we have to follow the two steps:

- Combination of glassy and/or rubbery polymer with solvent to prepare the polymeric blend.
- To develop the enhanced polymer blend by mixing polymeric blends with amines.

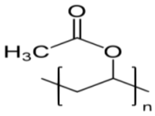
In order to find out compatibility of selected polymers, initial experimentation will be carried out to study blending behavior of polymers (Glassy & Rubbery) in different solvents and amines.



Polysulfone

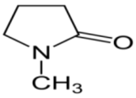


Polyethersulfone

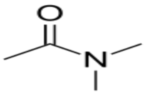


Polyvinyl acetate

Fig. 3. Structure of Polysulfone, Polyethersulfone and Polyvinyl acetate.

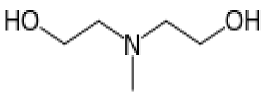


N-Methyl-2-pyrrolidone (NMP)

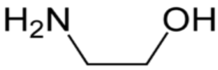


Dimethylacetamide (DMAc)

Fig. 4. Structure of N-Methyl-2-pyrrolidone (NMP) and Dimethylacetamide (DMAc).



Methyl diethanol amine (MDEA)



Mono ethanol amine (MEA)

Diethanol amine (DEA)

Fig. 5. Structure of Methyl diethanol amine (MDEA), Mono ethanol amine (MEA) and Diethanol amine (DEA).

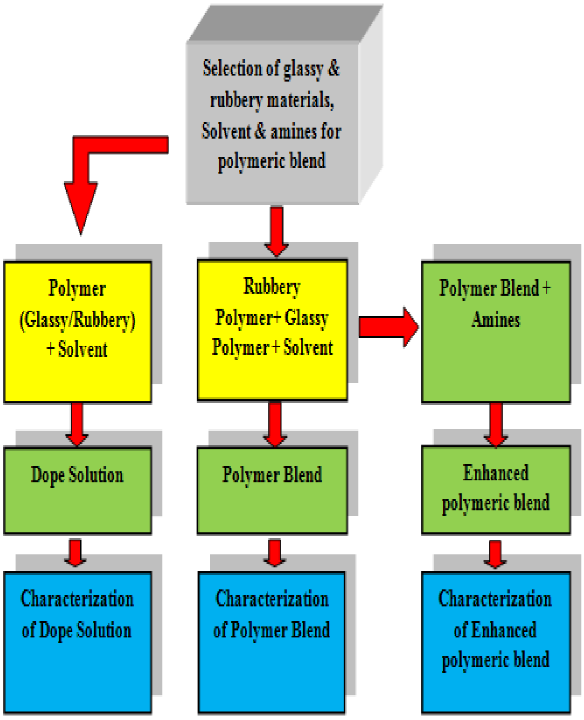


Fig. 6. Research Methodology.

In this process, experimentation on blending of glassy and rubbery polymer that is Polysulfone, Polyethersulfone and Polyvinyl acetate (Fig. 3) is carried out in two different solvents that is N-Methyl-2-pyrrolidone (NMP) and Dimethylacetamide (DMAc) (Fig. 4) and three different amines that is Methyl diethanol amine (MDEA), Mono ethanol amine (MEA) and Diethanol amine (DEA) (Fig. 5).The blending is 20% weight/weight. The solvent is 70%, polymer is 20% and amine is 10% of total weight. PES & PSF were pre heated overnight to remove any moisture content. Initially PVAc was allowed to dissolve in the solvent completely. Then glassy polymer was added. After the glassy and rubbery polymer are blend then we added the amine. Stirring was continued for 24 hour. Polymers and amines will be dissolved in a solvent at room temperature under continuous stirring to obtain a homogeneous mixture. Appearance, pH and viscosities of the blends are recorded. The sequence of research methodology as shown in Fig. 6.

IV. Discussion

The viscosity and pH relationship is polymeric blend of polyether sulfone, polysulfone, polyvinyl acetate, amines and solvents. The constants are:

- The viscosity of DMAc. in 20^{o}C @ 1.95 cp. The pH is 9.36.
- The viscosity of NMP in 20^{o}C & 50^{o}C is 1.7cp & 1.0cp respectively. The pH is 8.0-9.5.
- The viscosity of MDEA in 20^{o}C & 40^{o}C is 101cp & 33.8cp respectively. The pH is 10.7.
- The viscosity of MEA in 20^{o}C & 40^{o}C is 13.0cp & 6.5cp respectively. The pH is 12.0.
- The viscosity of DEA in 25^{o}C & 60^{o}C is 351.9cp & 53.8cp respectively. The pH is 11.5.
- The boiling point of DMAc. is 165^{o}C & flash point is 63^{o}C.
- The boiling point of NMP is 204.3^{o}C & flash point is 91^{o}C.
- The boiling point of MDEA is 247.3^{o}C.
- The boiling point of MEA is 159.6^{o}C.
- The boiling point of DEA is 271^{o}C.

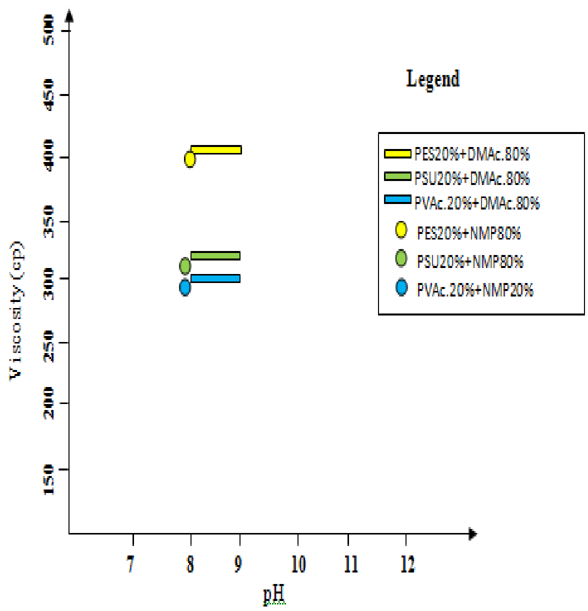
In Fig. 7, graph1, the cross plot of pH verses viscosity shows that the polymers (20%) PES, PSU, PVAc. in DMAc. solvent (80%). The pH are constant that is 8.00-9.00, but the viscosity is varies in PES, PSU, PVAc. polymers are 415cP, 300cP and 330cP respectively. In NMP solvent (80%) and the above polymers (20%), the pH are constant that is 8.00 but the viscosity is change in PES, PSU, PVAc. polymers are 400cP, 290cP and 315cP respectively.

In Fig. 7, graph 2 shows the blending behavior of PES, PSU and PVAc. in DMAc. and NMP in term of pH and viscosity. When the polymer(20%) of PVAc. 10% and PES 90% ,PVAc. 90% and PES 10% in DMAc. solvent(80%) the pH are constant that is 8.00-9.00, but the viscosity of this blend is 410cP and 335cP @30^0 C, 50rpm respectively. The blending of polymer(20%) of PVAc. 10% and PSU 90%, PVAc. 90% and PSU 10%, the pH are constant that is 8.00-9.00, but the viscosity of this blend is 310cP and 320cP respectively. In NMP solvent (80%), the polymer (20%) of PVAc. 10% and PES 90%, PVAc. 90% and PES 10%, PVAc. 10% and PSU 90%, PVAc. 90% and PSU 10%, the pH is

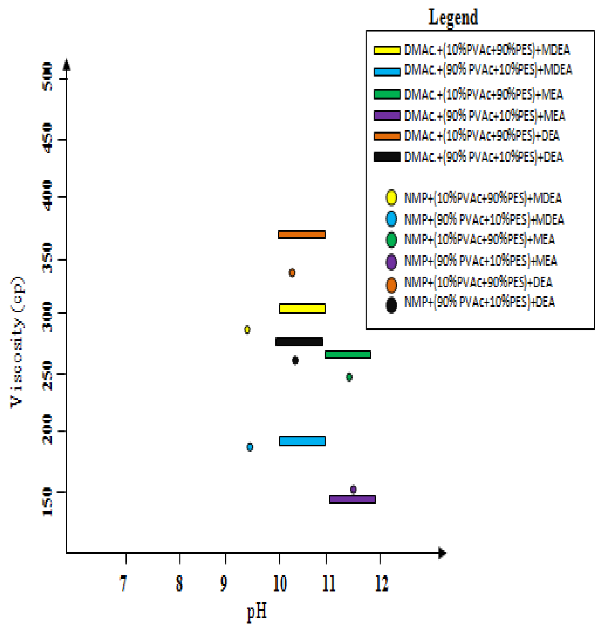
330cP, 295cP and 310cP respectively.

In Fig. 7, the graph 3 and 4 the blending behavior of PES, PSU, PVAc. polymers and amines in DMAc. and NMP solvent in terms of pH and viscosity. These graphs represent the blending, polymer(20%) of PVAc. 10% and PES 90%, PVAc. 90% and PES 10%, PVAc. 10% and PSU 90%, PVAc. 90% and PSU 10% ,these all are blended with 10% MDEA amine ,the pH are constant that is10.00-11.00, but the viscosities of these blends with amines are 308cP, 188cP, 195cP and 175cP respectively. When the same concentration of solvents and polymers, but the amine is MEA (10%) the pH are 11.00-12.00 and there viscosities are 265cP, 145cP, 150cP and 130cP respectively. When the DEA (10%) amine is blend in same concentration of above polymers and solvents the pH is 10.00-11.00 and the viscosities are 360cP, 265cP, 240cP and 250cP respectively.

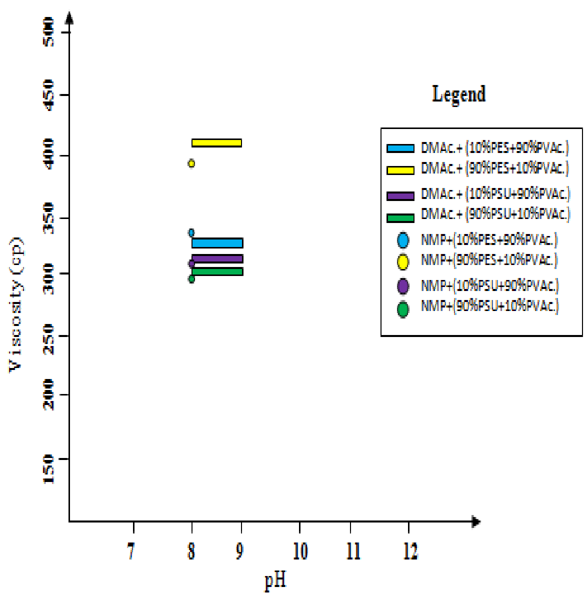
When the NMP solvent(70%) the polymer(20%) of PVAc.10% and PES 90%, PVAc. 90% and PES 10%, PVAc. 10% and PSU 90%, PVAc. 90% and PSU 10% blend with 10% MDEA amine, the pH of all these are 9.5 and the viscosities of these blends with amines is 285cP, 185cP, 195cP and 165cP respectively. The same above concentration of polymers and solvent in 10% MEA amine the pH is also constant 11.5, but the viscosities are 240cP, 140cP, 150cP and 120cP correspondingly. Again the same concentration of above mentioned polymers and solvents with 10% DEA amine even pH is 10.5, and then there viscosities of these blends with amines are 335cP, 255cP, 245cP, 235cP respectively.



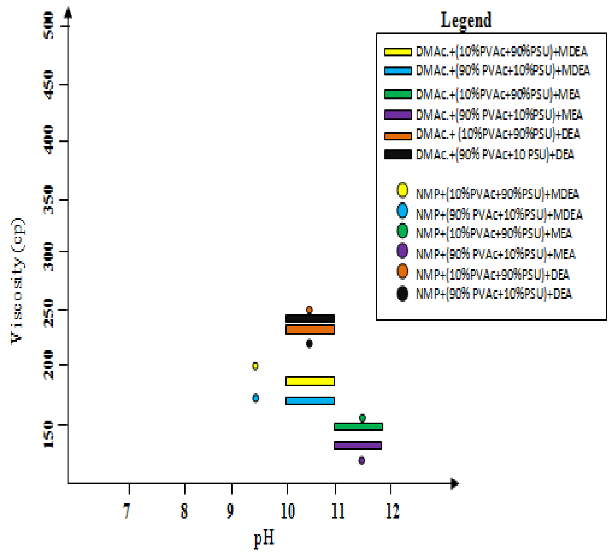
Graph 1: Blending Behavior of Pure PES, PSU & PVAc. in DMAc. & NMP



Graph 3: Blending Behavior of PES, PVAc. & Amines in DMAc. & NMP



Graph 2: Blending Behavior of PES, PSU & PVAc. in DMAc. & NMP



Graph 4: Blending Behavior of PSU, PVAc. & Amines in DMAc. & NMP

Fig. 7. Blending behavior of polymeric materials in terms of pH verses viscosity.

V. CONCLUSION

It is concluded that PES, PSU, PVAc. and amines blend in all compositions is miscible in NMP and DMAc solvent. A clear solution is obtained. All the polymeric blends are basic in nature, the minimum pH is 8.00 and maximum pH is 12.00. The viscosity of the polymeric blend, minimum is 120cP and maximum 415cP @ 30^{o}C, 50 rpm. With the change of solvent whatever the polymer is used the pH is same, but the viscosity is changing which can be used as a differentiate point. When the percentages of polymers are changing in the same solvent the pH is remaining same but the viscosity is variable. Therefore, difference in viscosity is showing the characteristics of blended polymers are changing. When the using DEA, MDEA in the DMAc. with different percentage of polymers the pH is same because the diethyl, methyl diethyl is decrease the bascity of amine. On the other hand MEA is used in the same solvent DMAc. With the different percentage of polymer the significant increase in pH.

The present research shows how to develop a polymer blend for the development of the current need of having high permeability and selectivity membrane for removal of CO_2 from natural gas. The developed polymer blend membranes have improved flexibility, reduced cost, improved process ability, and enhanced selectivity and/or permeability compared to the comparable polymer membranes that comprise a single polymer. It will be possible to develop polymeric blend membrane for separating high pressure gas streams at their processing pressure. This advantage could offer cost savings that may provide a new incentive for polymeric blend membranes. This result opens a new tool for studying gas separation by polymeric blend membranes. The impact of this breakthrough will be able to monetize the stranded gas wells having high CO_2 content. Therefore, this will increase the economic growth in gas industry of the country.

ACKNOWLEDGEMENT

I would like to express my deep and sincere gratitude to the Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia for their encouragement and support during my conference paper. I am very thankful to NED University of Engineering & Technology, Karachi, Pakistan, who gives me financial support for my higher studies.

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