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Blending Behavior of Polysulfone, Polyvinyl Acetate & Amines in Dimethyl Acetamide Solvent

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***Abstract*- In this paper, research will be carried out to classify the blending behavior of glassy and rubbery polymer in solvent with amines. Commercially preface of a polymer prepared from a new monomer is uncertain and enormously expensive. A strategy to introduce new products into the market without a large investment is to take dissimilar polymers, amines and blend them together to make a new product with unique properties. The blending of polyvinyl acetate, polysulfone and diethanol amine, methyl diethanol amine, mono ethanol amine are examined with dimethyl acetamide solvent, which gives the results of appearance, pH and viscosity values by using measuring device viscometer and general pH testing technique. Through getting these results, the intrinsic miscibility of the mixture was finally established which shows that the homogenous or heterogeneous blends are depending on the blend preparation method and percentage of polymers and amines. The achievement of this advance has been restricted, because the mechanical properties of the blend with amines are classically worse than a simple mixing law would predict.**

***Keywords* - Polyvinyl Acetate; Polyether sulfone; Dimethyl Acetamide Solvent; Amines; Blending.**

I. Introduction

Polymer blending with amines is taken into account as time and cost effective methodology to develop materials with advantageous properties.

Polymer Blend is a mixture of two polymers or copolymers. Polymer blends are presently more important in scrupulous sectors of polymer industry [1], as they will commonly meet performance requirements that cannot be satisfied by the currently accessible commodity polymers. Accordingly, their attractiveness will increases with the increasing demands for this category of materials. As a logical consequence, several studies are dedicated to polymer blends, with special stress on their mechanical and thermal behavior. It is probable to acquire polymer blends of more advantageous properties by mixing miscible polymers, and hence it is very important to examine the factors disturbing the miscibility of polymer mixtures. The miscibility words illustrate the homogeneity of polymer mixtures at some temperatures.

Previous research found that polymeric membrane having sensible repute in natural gas purification [1,13,14]. During this research study we prepare the polymer blend of polymeric membrane by the combination of glassy and/or rubbery polymer and adding up the amines. This method ends up in 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 increase the selectivity, permeability, chemical stability and mechanical strength. However, blending of glassy and rubbery polymers with amines has not been studied.

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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	[2]
2	2006	PU based PAI/PEI (Glassy/Glassy) blend	CO_2		[3]
3	2006	PDMS/PU (Rubbery/Rubbery)	Gas mixture	Cross-linked	[4]
4	2006	PVDF/PES (Glassy/Glassy)		studied effect of solvent, polymer composition & morphology	[5]
5	2009	PVAm/PVA with porous PES support	Facilitated CO_2 transport	Ultra-thin membrane with good strength, constancy and permeability/selectivity	[6]
6	2008	PI/PES (Glassy/Glassy) blend MMM	N_2/O_2		[7]
7	2010	PDMS/PU (Rubbery/Rubbery)	Toluene/methanol	per vaporization	[8]
8	2010	PEG/PDMS	CO_2 separation		[9]
9	2010	CA(porous)/PU (Glassy/Rubbery)	Micro filtration		[10]
10	2010	PI/PES (Glassy/Glassy)	N_2/ O_2		[11]
11	2011	Matrimid/ SPEEK	Separation of CO_2	Cross-linked for anti-plasticization	[12]
12	2011	PI/PSF (Glassy/Glassy)	CH_4/ CO_2	studied effect of solvents	[13]
13	2011	PEI/PVP	CO_2/CH_4, CO_2/N_2	Carbon hollow fiber membrane	[14]
14	2012	PES (PVP or PEG) with PDMS coating	toulene/water	per vaporization	[15]
15	2012	PVAc./PU with PEO/PPO	Gas mixture	increased CO_2 permeability	[16]
16	2012	PIM-1/ Matrimid	CO_2/CH_4 , CO_2/N_2	increased selectivity	[17]

Abbreviations: PAI=polyamide imide, PDMS=polydimethyl siloxane, 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, PEA=aromatic polyether amide, PPO=polypropylene oxide, PVA=polyvinyl alcohol, PVAc=polyvinyl acetate, PVAm=polyavinylamine, PVDF=polyvinylidene fluoride, PVP=polyvinyl, poly(ether-ether-ketone), CA=cellulose acetate, SPEEK=sulfonated aromatic.

The detailed composition of polymers and solvents is given in this table 2. On the basis of these reports, the advance study will be proceeded to study the blending behavior of polymers.

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Table II
Different Studies regarding Polymer Blend Composition

Polymer A	Polymer B	Solvent	Blend composition	Ref.
PSU (%)	PI (%)	(DCM/NMP) (%) 80/20,50/50, 20/80	25 g polymer is used.	[13]
100	0			
95	5			
90	10			
85	15			
80	20			
PSU (%)	PI (%)	Methylene chloride (DCM)	5 wt % of solution	[18]
80	20			
50	50			
20	80			
PES (%)	PI (%)	NMP	35% , 30%, 26% in solvent, respectively	[2]
80	20			
50	50			
20	80			
PDMS (%)	PU (%)	THF	20% in solvent	[8]
0	100			
20	80			
40	60			
60	40			
80	20			
100	0			
PSU (%)	PVAl (%)	DMF	10 % in solvent	[16]
100	0			
95	5			
90	10			
85	15			

Table III
Different Amines Comparison [20]

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 ammonical	Mild ammonical odor	Ammonical 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

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The amine solution has the potential to purify the natural gas having acid gas. Amine has a natural affinity for each Carbon dioxide and Hydrogen Sulphide allowing this to be a very capable and successful removal process[19]. The tables 3 show the comparison of different amines properties.

II. BACKGROUND

The separation ways for removing greenhouse emissions that is CO_2 will either be bulk or trace removal counting on the applying. The principal factors that are usually considered when selecting a suitable separation schemes are product purity, feed and products gas partial pressure requirements, operating temperature, energy requirements and also the presence of impurities among the gas. Fig.1 shows the approximate ranges of application of various sorts of gas treating processes for greenhouse emission (CO_2) removal within the feed gas.

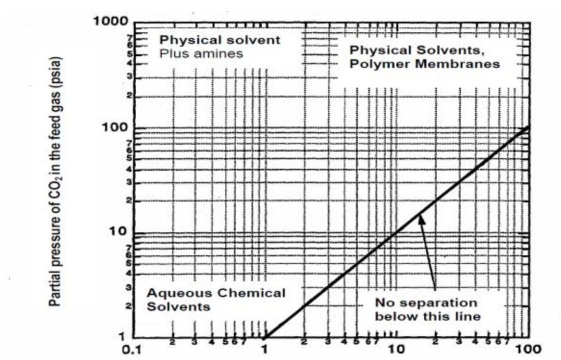

Figure1: Partial pressure of CO_2 in the product gas (psia)

Amine-containing chemical solvents are usually favored when the partial pressure of CO_2 within the feed gas is comparatively low or once CO_2 reduced to a very low concentration within the treated gas. Physical solvents be use at high CO_2 pressures within the feed gas and when deep CO_2 removal isn't needed.

In addition, the invention and development of recent polymers blend has created separation of gases by membranes competitive in relation to the conventional ways of scrubbing using physical or chemical solvents. As among the gas scrub process, the absorption of the reactive gas (*e.g*. CO2) may be enhanced by the adding of reactive carrier to the matrix. As a result, more increase within the mass transport may 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 [23].

From figure 2, polymer blending offers time and cost effective technique to develop materials with useful properties. So, consequence of blending of a glassy and a rubbery polymer with different amines solutions, for that purpose to enhance the separation ability for CO_2/CH_4 mixture. The amine solution has the prospective to get rid of impurities the natural gas having acid gas. Amine has a natural attraction for both CO_2 and H_2S allowing this to be a very well-organized and valuable removal process and also with topping of amines on the performance of polymeric membrane should be study so that a membrane with high selectivity and high permeability might be developed

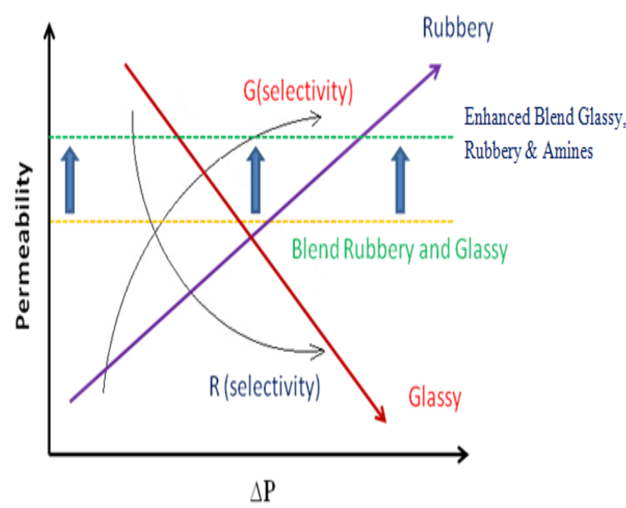

Figure 2: Current Trend of Enhanced Polymeric Blend Membrane

A. Materials for Gas Separation Membrane

The selection of material membrane is the most important factor for Gas Separation.

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Chemical interaction between a membrane material and a gas penetrate determined the separation efficiency of a membrane separation process [21].

The choice of material is based on the cost-effectiveness and applications. The most important necessities of effective separation material are: [22,24]

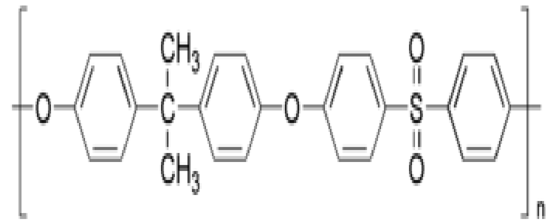
1. Engineering feasibility.
2. Good chemical resistance.
3. High separation efficiency with reasonable high flux.
4. Good mechanical stability.
5. High thermal stability.
6. Low cost.

III. METHODOLOGY

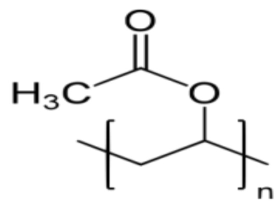
Polysulfone (PSF) Udel® P-1800 having a glass transition temperature (T_g) of 185 ^{0}C was acquired from Solvay Advanced **Polymers;** L.L.C, U.S. PSU was in minced form. **Polyvinyl acetate** (PVAc.) average M_w ~100,000 by GPC, beads from Sigma Aldrich having a glass transition temperature (T_g) 30^{0}C. Dimethyl acetamide (DMAc.) solvent and methyl diethanol amine, diethanol amine, mono ethanol amine with a purity of 99.99% was purchased from Merck.

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

In this process, experimentation on blending of glassy and rubbery polymer that is Polysulfone and Polyvinyl acetate (figure 2) is carried out in solvent that is Dimethylacetamide (DMAc) (figure 3) and three different amines that is Methyl diethanol amine (MDEA), Mono ethanol amine (MEA) and Diethanol amine (DEA) (Figure 4).The blending is 20% weight/weight. The solvent is 70%, polymer is 20% and amine is 10% of total weight. PSU were pre heated during the night to remove any moisture content. Initially PVAc .was allowed dissolving in the DMAc. Solvent completely. Then glassy polymer was added. Later than the glassy and rubbery polymer blend then we added the 10% amine. Stirring was continuous for 24 hours. Polymers and amines will be dissolving in a solvent at room temperature under continuous stirring to obtain a homogeneous mixture. To obtain a clear solution followed by bath sonication in Transsonic Digital S, Elma® for 1 hr. for the purpose of degassing. Appearance, pH and viscosities of the blends are recorded.



Polysulfone



Polyvinyl acetate

Figure 3: Structure of Polysulfone and Polyvinyl acetate.

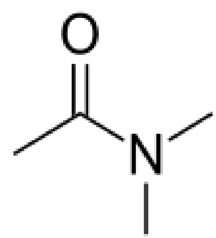
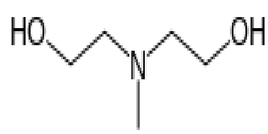
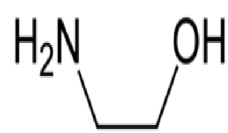


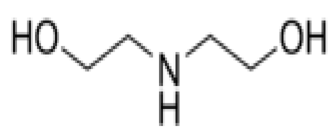
Figure 4: Structure of Dimethylacetamide (DMAc).



Methyl diethanol amine (MDEA)



Mono ethanol amine (MEA)



Diethanol amine (DEA)

Figure 4: Structure of Methyl diethanol amine (MDEA), Mono ethanol amine (MEA) and Diethanol amine (DEA).

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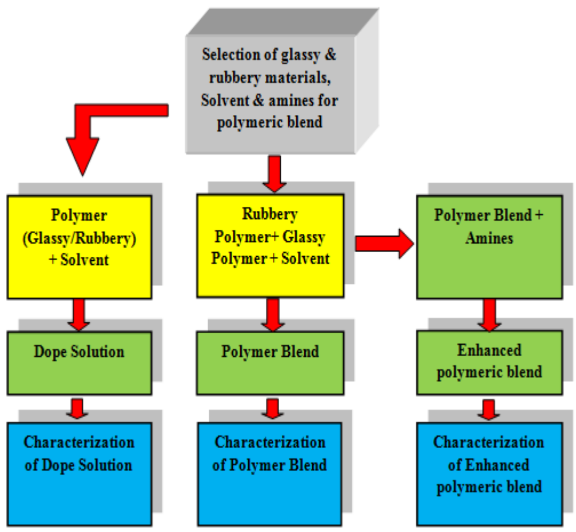

Figure 5: Research Methodology

IV. DISCUSSION

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

- The viscosity of DMAc. in 20°C @ 1.95 cp. The pH is 9.36.
- The viscosity of MDEA in 20°C & 40°C is 101cp & 33.8cp respectively. The pH is 10.7.
- The viscosity of MEA in 20°C & 40°C is 13.0cp & 6.5cp respectively. The pH is 12.0.
- The viscosity of DEA in 25°C & 60°C is 351.9cp & 53.8cp respectively. The pH is 11.5.
- The boiling point of DMAc. is 165°C & flash point is 63°C.
- The boiling point of MDEA is 247.3°C.
- The boiling point of MEA is 159.6°C.
- The boiling point of DEA is 271°C.

In graph1, the cross plot of pH verses viscosity shows that the pure polymers (20%) PSU, PVAc. in DMAc. Solvent (80%). The pH are constant that is 8.00-9.00, but the viscosity is varies in PSU, PVAc. polymers are 300cP and 400cP respectively.

In graph 1, also show the blend of PSU 20% and amines (MDEA, MEA, DEA) 10% in a 70% DMAc. Solvent all the pH are change in blend due to the addition of amine. The pH becomes are MDEA and DEA blend is 10.00-11.00 however, the pH of MEA is 11.00-12.00 and the viscosity of MEA, MDEA, DEA blend in PSU are 170cP, 215cP and 255cP respectively due to the original viscosity of amines are DEA>MDEA>MEA.

The graph 2 shows the blending behavior of PVAc. and PSU in DMAc. in term of viscosity and pH. When the polymer (20%) of PVAc. 5% and PSU 95% in DMAc. solvent (80%) the pH are constant that is 8.00-9.00, but the viscosity of this blend is 305cP @30^0 C, 50rpm respectively. The blending of polymer(20%) of PVAc. 10% and PSU 90%, PVAc. 15% and PSU 85%, PVAC. 80% and PSU 20%, PVAc. 75% and PSU 25% in DMAc. solvent(80%) all the pH are constant that is 8.00-9.00, but the viscosity of this blend is 310cP, 315cP, 320cP and 325cP respectively. Its means that there is no change occur in pH when the blend is occur PSU and PVAc. but the viscosity is increases when the PVAc. percentage is increases in PSU due to the pure PVAc. viscosity is greater than the PSU viscosity.

In graph 3, 4 and 5 shows the blending behavior of three components that is PSU, PVAc. polymers and amines in DMAc. Solvent in terms of pH and viscosity. These graphs represent the blending, polymer (20%) of PVAc. 5% and PSU 95%, PVAc. 10% and PSU 90%, PVAc. 15% and PSU 85%, PVAc. 20% and PSU 80%, PVAc. 25% and PSU 75%, these all are blended with 10% amine in a 70% DMAc. solvent. The pH are constant in different percentage of polymer its mean that the pH are independent of increasing the percentage of polymer. The pH becomes when the amine is MDEA and DEA is 10.00-11.00, but the viscosities of these blends with MDEA amine are 220cP, 225cP, 230cP, 235cP and 240cP respectively and DEA amine the viscosities of these different percentage of polymer are 260cP, 265cP, 270cP, 275cP and 280cP 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 175cP, 180cP, 185cP, 190cP and 195cP respectively.

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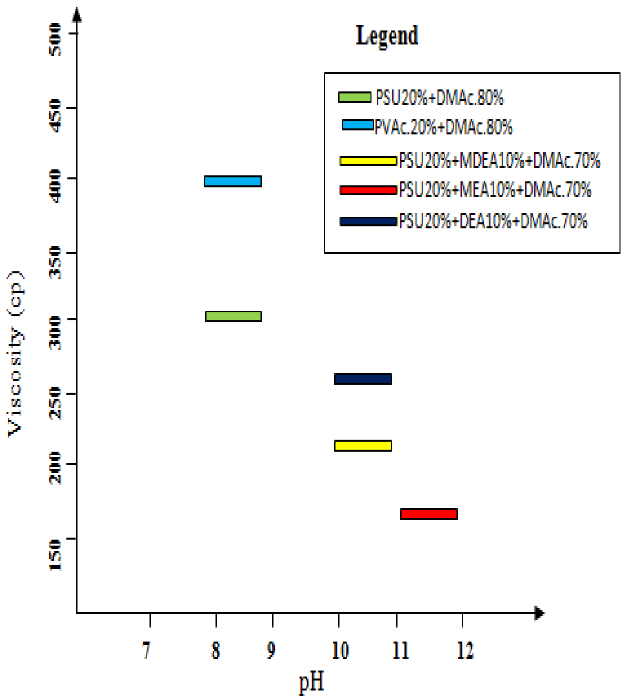
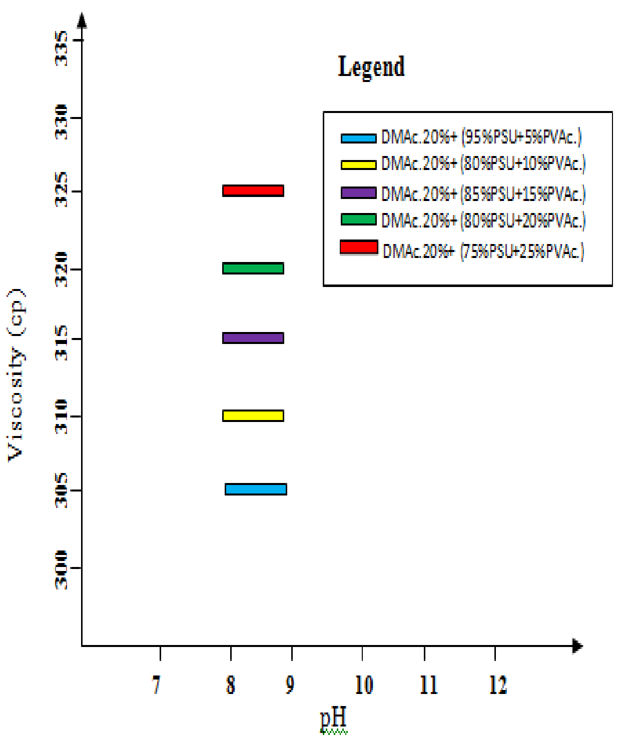
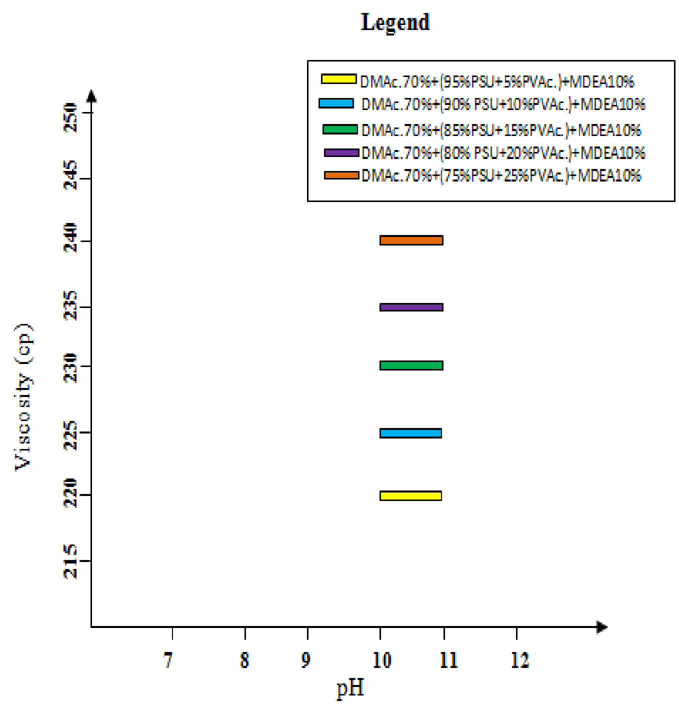


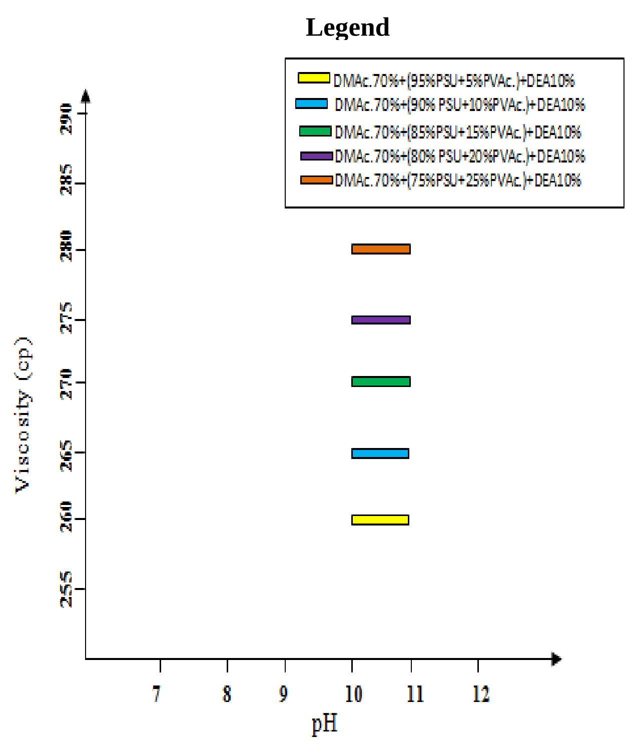
Graph 1: Blending Behavior of Pure PSU, PVAc. & Amines in DMAc. Solvent



Graph 2: Blending Behavior of PSU & PVAc. in DMAc. Solvent



Graph 3: Blending Behavior of PSU, PVAc. & MDEA in DMAc. Solvent



Graph 4 : Blending Behavior of PSU, PVAc. & DEA in DMAc. Solvent

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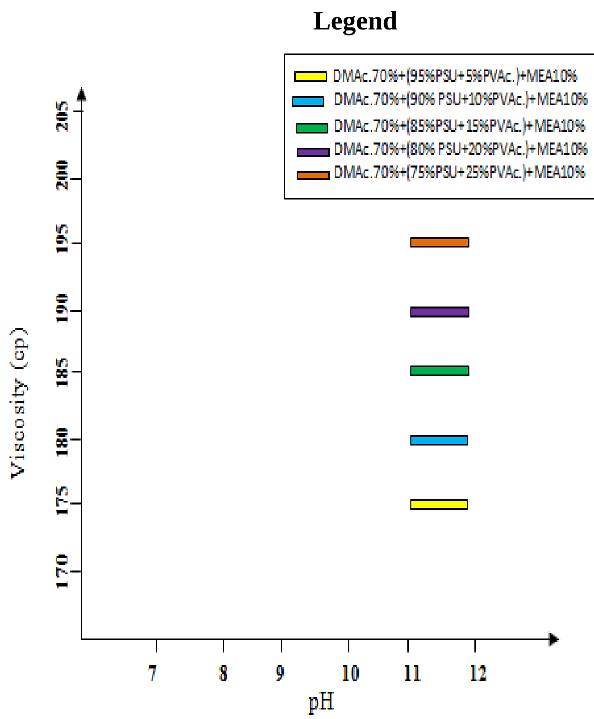

Graph 5 : Blending Behavior of PSU, PVAc. & MEA in DMAc. Solvent

V. CONCLUSION

It is concluded that PSU, PVAc. and amines blend in all different compositions is miscible in DMAc. solvent. A clear solution is obtained. All the PSU, PVAc. polymeric blends with or without amines are basic in nature, the pH range between is 8.00 to 12.00. The viscosity of the polymeric blend, minimum is 175cP and maximum 400cP @ 30^{o}C, 50 rpm. When the percentages of polymers are changing in the DMAc 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 since 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 viscosity is increase when the PVAc. percentage is increases in PSU due to the pure PVAc. viscosity is greater than the PSU. The most significant impact occurs the viscosity is decreases when the amine is blend in PVAc. and PSU polymeric blend due to the original viscosity of amines are lesser MEA<MDEA<DEA.

The present research shows how to develop an enhanced 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 enhanced polymer blend membranes have improved flexibility, reduced cost, improved process ability, and enhanced permeability and/or selectivity compared to the comparable polymer membranes that comprise a single polymer. It shall be probable 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. The impact of this breakthrough will be able to monetize the stranded gas wells having high CO_2 content. Hence, this will increase the economic growth in gas industry.

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