

Research Article

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

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Abstract: In this study, 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: Amines, blending, dimethyl acetamide solvent, polyvinyl acetate, polysulfone

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 (Miles and Rostami, 1992), as they will commonly meet performance requirements that cannot be satisfied by the currently accessible commodity polymers. Accordingly, their attractiveness will increase 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 (Miles and Rostami, 1992; Rafiq *et al.*, 2011; Salleh and Ismail, 2011). 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 CO₂/CH₄ 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. In Table 1 shows the different studies regarding the glassy/glassy and rubbery/rubbery materials. 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 2. On the basis of these reports, the advance study will be proceeded to study the blending behavior of polymers.

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 (Kerry, 2007). Amine will enhanced the properties of polymeric blend. Table 3 show the comparison of different amines properties.

LITERATURE REVIEW

The separation ways for removing greenhouse emissions that is CO₂ 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

Table 1: Different studies regarding on blend membrane

Year	Polymers	System	Remarks	References
2002	PES/PI (glassy/glassy) coated with PDMS	Gas separation	Hollow fiber	Kapantaidakis <i>et al.</i> (2002)
2006	PU based PAI/PEI (glassy/glassy) blend	CO ₂		Kim <i>et al.</i> (2006)
2006	PDMS/PU (rubbery/rubbery)	Gas mixture	Cross-linked	Tremblay <i>et al.</i> (2006)
2006	PVDF/PES (glassy/glassy)		Studied effect of solvent, polymer composition and morphology	Wu <i>et al.</i> (2006)
2009	PVAm/PVA with porous PES support	Facilitated CO ₂ transport	Ultra-thin membrane with good strength, constancy and permeability/selectivity	Deng <i>et al.</i> (2009)
2008	PI/PES (glassy/glassy) blend MMM	N ₂ /O ₂		Ismail <i>et al.</i> (2008)
2010	PDMS/PU (rubbery/rubbery)	Toluene/methanol	Per vaporization	Lue <i>et al.</i> (2010)
2010	PEG/PDMS	CO ₂ separation		Reijerkerk <i>et al.</i> (2010)
2010	CA (porous) /PU (glassy/rubbery)	Micro filtration		Zavastin <i>et al.</i> (2010)
2010	PI/PES (glassy/glassy)	N ₂ /O ₂		Han <i>et al.</i> (2010)
2011	Matrimid/SPEEK	Separation of CO ₂	Cross-linked for anti-plasticization	Khan <i>et al.</i> (2011)
2011	PI/PSF (glassy/glassy)	CH ₄ /CO ₂	Studied effect of solvents	Rafiq <i>et al.</i> (2011)
2011	PEI/PVP	CO ₂ /CH ₄ , CO ₂ /N ₂	Carbon hollow fiber membrane	Salleh and Ismail (2011)
2012	PES (PVP or PEG) with PDMS coating	Toulene/water	Per vaporization	Salehi Shahrabi <i>et al.</i> (2011)
2012	PVAc./PU with PEO/PPO	Gas mixture	Increased CO ₂ permeability	Semsarzadeh and Ghalei (2012)
2012	PIM-1/matrimid	CO ₂ /CH ₄ , CO ₂ /N ₂	Increased selectivity	Yong <i>et al.</i> (2012)

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

Table 2: Different studies regarding polymer blend composition

Polymer A	Polymer B	Solvent	Blend composition	References
PSU (%)	PI (%)	(DCM/NMP) (%) 80/20, 50/50, 20/80	25 g polymer is used	Rafiq <i>et al.</i> (2011)
100	0			
95	5			
90	10			
85	15			
80	20			
PSU (%)	PI (%)	Methylene Chloride (DCM)	5 wt % of solution	Kapantaidakis <i>et al.</i> (1996)
80	20			
50	50			
20	80			
PES (%)	PI (%)	NMP	35 , 30 and 26% in solvent, respectively	Kapantaidakis <i>et al.</i> (2002)
80	20			
50	50			
20	80			
PDMS (%)	PU (%)	THF	20% in solvent	Lue <i>et al.</i> (2010)
0	100			
20	80			
40	60			
60	40			
80	20			
100	0			
PSU (%)	PVAI (%)	DMF	10 % in solvent	Semsarzadeh and Ghalei (2012)
100	0			
95	5			
90	10			
85	15			

of impurities among the gas. Figure 1 shows the approximate ranges of application of various sorts of gas treating processes for greenhouse emission (CO₂) removal within the feed gas.

Amine-containing chemical solvents are usually favored when the partial pressure of CO₂ within the feed gas is comparatively low or once CO₂ reduced to a very low concentration within the treated gas. Physical

solvents are use at high CO₂ pressures within the feed gas and when deep CO₂ 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

Table 3: Different amines comparison (Nicholas, 2003)

Properties	Amine				
	DEA	DGA	MEA	MDEA	DIPA
Molecular Wt.	105.14	105.14	61.08	141	101.19
B.P (°C)	221	515.10	171	247	85
Solubility in H ₂ O	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	0.30-0.35	0.30-0.35	0.30-0.35	Unlimited	0.41-0.61

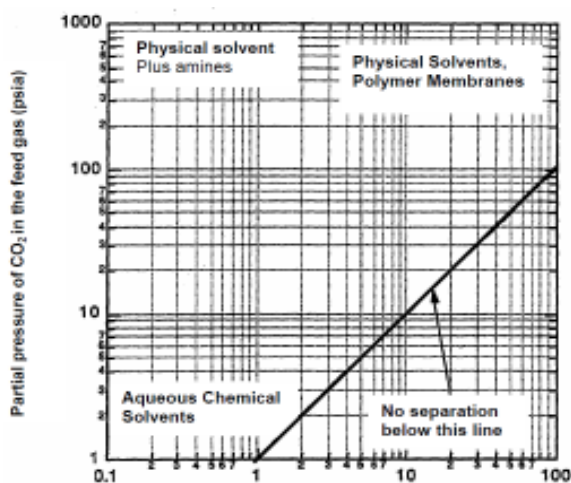


Fig. 1: Partial pressure of CO₂ in the product gas (psia)

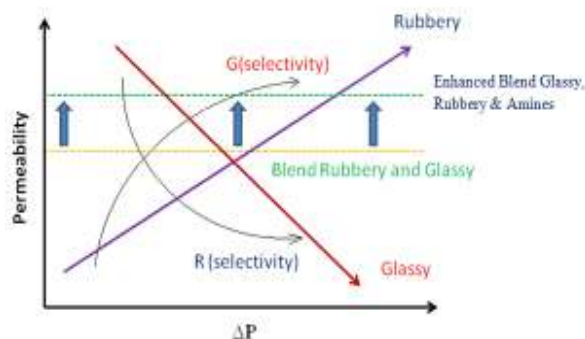


Fig. 2: Current trend of enhanced polymeric blend membrane

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 CO₂-amine solutions over the years due to its important industrial application for the removal of CO₂ from gas streams. The overall reaction between CO₂ and primary or secondary amines is:



where, R represents the functional groups (for MEA, R₁ = -H, R₂ = -CH₂CH₂OH; for DEA, R₁ = R₂ = -CH₂CH₂OH).

The Dankwerts' zwitterions mechanism has recently become one of the most widely accepted mechanism for primary and secondary amine reaction with CO₂ (Blauwhoff *et al.*, 1984).

From Fig. 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 CO₂/CH₄ 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 CO₂ and H₂S 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.

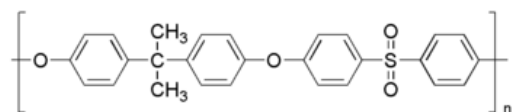
Materials for gas separation membrane: The selection of material membrane is the most important factor for Gas Separation. Chemical interaction between a membrane material and a gas penetrate determined the separation efficiency of a membrane separation process (Rufford *et al.*, 2012).

The choice of material is based on the cost-effectiveness and applications. The most important necessities of effective separation material are: (Peters *et al.*, 2011; Davison and Thambimuthu, 2004):

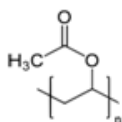
- Engineering feasibility
- Good chemical resistance
- High separation efficiency with reasonable high flux
- Good mechanical stability
- High thermal stability
- Low cost

METHODOLOGY

Polysulfone (PSF) Udel® P-1800 having a glass transition temperature (T_g) of 185°C was acquired

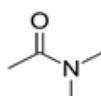


(a) Polysulfone

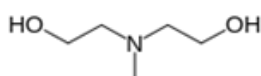


(b) Polyvinyl acetate

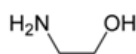
Fig. 3: Structure of polysulfone and polyvinyl acetate



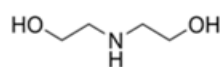
(a) Structure of Dimethylacetamide (DMAc)



(b) Methyl Diethanol Amine (MDEA)



(c) Mono Ethanol Amine (MEA)



(d) Diethanol Amine (DEA)

Fig. 4: Structure of Methyl Diethanol Amine (MDEA), Mono Ethanol Amine (MEA) and Diethanol Amine (DEA)

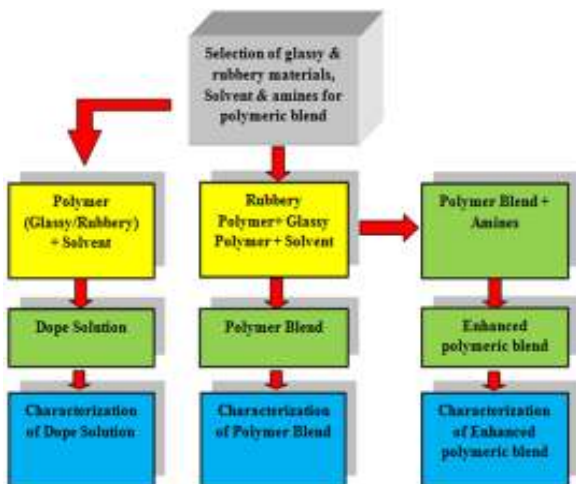


Fig. 5: Research methodology

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°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 and Rubbery) in DMAc. Solvent and amines.

In this process, experimentation on blending of glassy and rubbery polymer that is Polysulfone and Polyvinyl acetate (Fig. 2) is carried out in solvent that is Dimethylacetamide (DMAc) (Fig. 3) and three different amines that is Methyl Diethanol Amine (MDEA), Mono Ethanol Amine (MEA) and Diethanol Amine (DEA) (Fig. 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 h. 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 h. for the purpose of degassing. Appearance, pH and viscosities of the blends are recorded. The research methodology is defined in Fig. 5.

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 and 40°C is 101 and 33.8 cp, respectively. The pH is 10.7.
- The viscosity of MEA in 20 and 40°C is 13.0 and 6.5 cp, respectively. The pH is 12.0.
- The viscosity of DEA in 25 and 60°C is 351.9 and 53.8 cp, respectively. The pH is 11.5.
- The boiling point of DMAc., is 165°C and 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 Fig. 6, 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 300 and 400 cP, respectively. In Fig. 6,

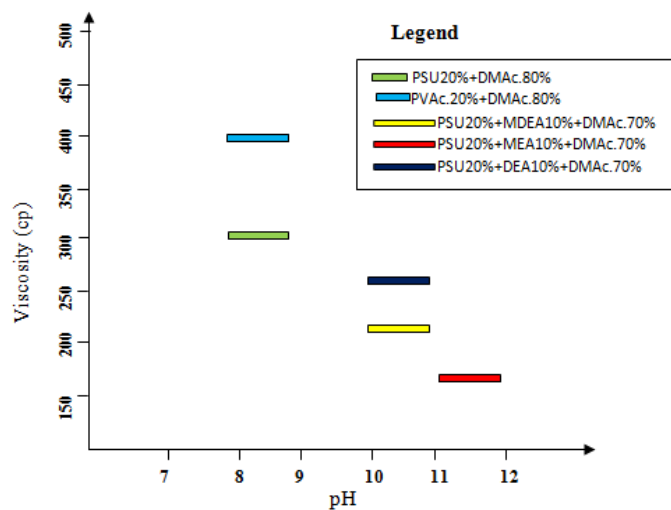


Fig. 6: Blending behavior of pure PSU, PVAc, and amines in DMAc. solvent

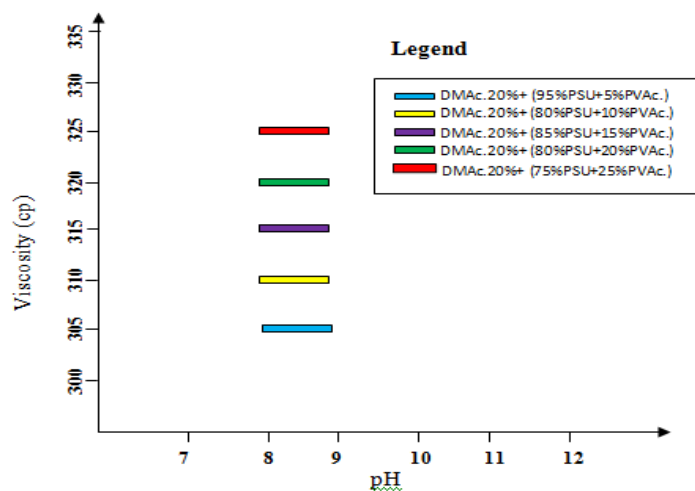


Fig. 7: Blending behavior of PSU and PVAc in DMAc. solvent

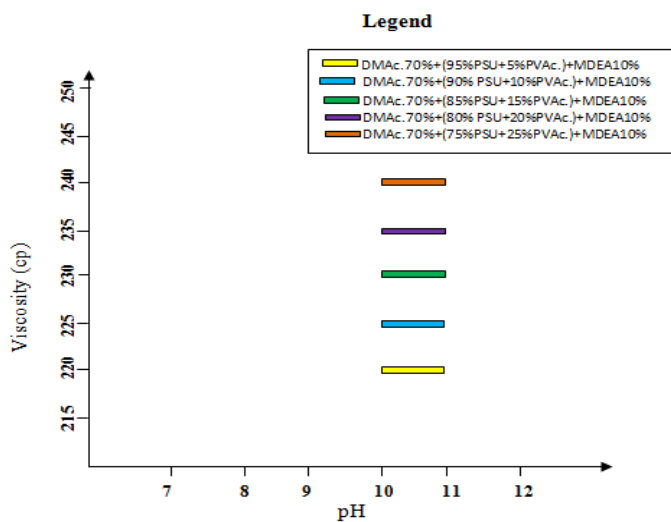


Fig. 8: Blending behavior of PSU, PVAc, and MDEA in DMAc. solvent

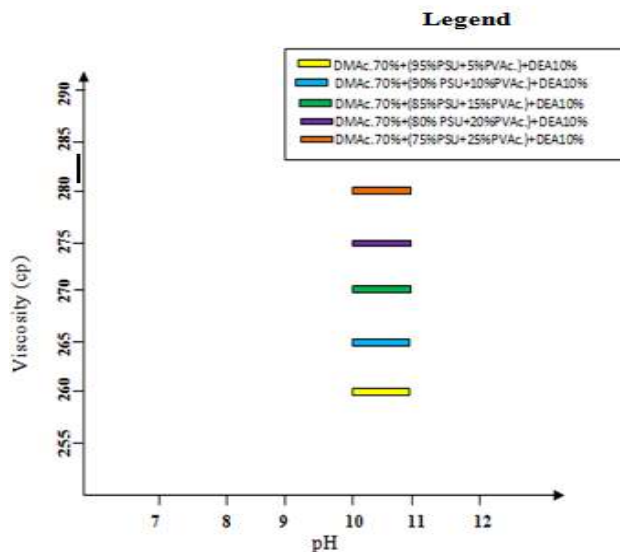


Fig. 9: Blending behavior of PSU, PVAc. and DEA in DMAc. solvent

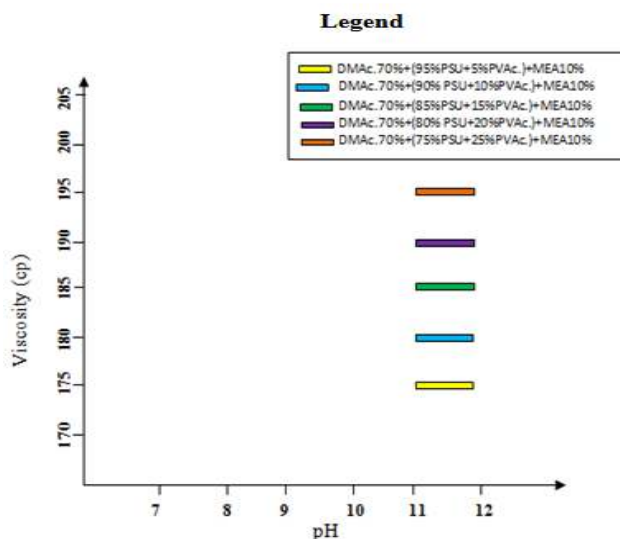


Fig. 10: Blending behavior of PSU, PVAc. and MEA in DMAc. solvent

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 170, 215 and 255 cP, respectively due to the original viscosity of amines are DEA>MDEA>MEA.

The Fig. 7 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 305 cP @30°C, 50 rpm, 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 310, 315, 320 and 325 cP, 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 Fig. 8 to 10 shows the blending behavior of three components that is PSU, PVAc. polymers and amines in DMAc. Solvent in terms of pH and viscosity. These Figures 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 220, 225, 230, 235 and 240 cP, respectively and DEA amine the viscosities of these different percentage of polymer are 260, 265, 270, 275 and 280 cP, 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 175, 180, 185, 190 and 195 cP, respectively.

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 400 cP @ 30°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 basicity 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 CO₂ 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 CO₂ content. Hence, this will increase the economic growth in gas industry.

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