

Research Article**FTIR Study of Enhanced Polymeric Blend Membrane with Amines**

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Abstract: In this study, research will be carried out to identify the functional group behavior of glassy and rubbery polymeric blend membrane with amines. Polymeric blend membranes with different blending ratios were prepared and the developed membranes were characterized by FTIR to see the effect of blend ratio on different functional groups. The developed membranes are flat dense sheet membrane of 20% wt/wt. The pure and blend membrane polysulfone, polyethersulfone, polyvinyl acetate with different composition, with 10% methyl diethanol amine, mono ethanol amine, diethanol amine are developed with dimethyl acetamide solvent. Fourier Transform Infrared (FTIR) spectroscopy was utilized to study the interaction between two polymers and to analyze the type of bonding present. To observed frequencies were assigned to various mode of vibration in terms of fundamentals and combination. These spectral changes indicated the existence of molecular interaction among the enhanced polymeric blends; highlight the compatible nature among each other.

Keywords: Amines, FTIR spectra, polyethersulfone, polymeric blend membrane, polysulfone, polyvinylacetate

INTRODUCTION

Recent literature surveys reveal an increasing number of polymers, copolymers and blends that are being considered as potential materials that can be used to modify membrane morphology; (Lloyd, 1985; Xu and Qusay, 2004). The blending technique not only provides improved chemical and thermal stability but is also efficient enough to improve the perm-selective properties with economical viability. Polymer blending with amines is considered as time and cost effective method to develop materials with desirable properties (Yoo *et al.*, 2013). A number of glassy and rubbery blend membranes are reported in literature e.g., PC/PSF (Acharya *et al.*, 2008), PU/PVAc (Semsarzadeh and Ghalei, 2012), PS/PPO (Kim *et al.*, 1997) and PBI/Matrimid (Hosseini *et al.*, 2008). Khan *et al.* (2011) successfully suppressed the plasticization behavior of polymeric membrane even at high pressure up to 40 bar for CO₂/CH₄ separation by blending SPEEK/Matrimid.

The amine solution has the capability to purify the natural gas having acid gas. Amine has a natural affinity for both Carbondioxide and Hydrogen Sulphide allowing this to be a very efficient and effective removal processes (Kerry, 2007).

Poly Vinyl Acetate (PVAc) is an important polymer, exhibiting piezoelectric, pyro-electric and ferroelectric properties (Kroschwitz, 1989). The typical advantages of PVAc. Are flexibility, formability and low density. Polyvinyl acetate is a rubbery synthetic polymer and it is prepared by polymerization of vinyl

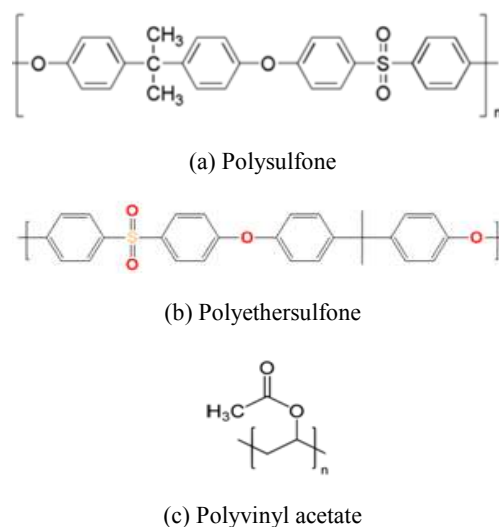


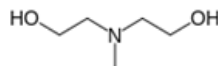
Fig. 1: Structure of polysulfone, polyethersulfone and polyvinyl acetate

acetate monomer, also known as VAM. Partial or absolute hydrolysis of the polymer is used to prepare polyvinyl alcohol. The PVAc. polymers are found to have wide applications but only limited studies have been reported so far (Samy *et al.*, 2007; Prabakaran, 1990).

Polyethersulfone (PES), Polysulfone (PSF) possesses outstanding thermal, oxidative and hydrolytic stability along with excellent flexibility and strength, high resistance to extreme pH, good mechanical and film-forming properties (Mark, 2004).



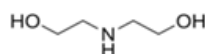
Fig. 2: Structure of Dimethylacetamide (DMAc)



(a) Methyl Diethanol Amine (MDEA)



(b) Mono Ethanol Amine (MEA)



(c) Diethanol Amine (DEA)

Fig. 3: Structure of Methyl Diethanol Amine (MDEA), Mono Ethanol Amine (MEA) and Diethanol Amine (DEA)

Table 1: FTIR spectra of pure PSU

PSU spectra	Wave number cm^{-1}
S = O symmetric stretch	1150, 1307
CSO ₂ C asymmetric stretch	1322
C-O asymmetric stretch	1244, 1260-1000
C ₆ H ₆ ring stretch	1587-1489
OH aliphatic and aromatic stretch	2886, 2938 and 2971

Table 2: FTIR spectra of pure PVAc.

PVAc. spectra	Wave number cm^{-1}
C = O stretch	1736, 1760-1670
C-O asymmetric stretch	1244, 1260-1000
C-H phenyl ring substitution band	850, 870-675

Table 3: FTIR spectra of pure PES

PES spectra	Wave number cm^{-1}
S = O symmetric stretch	1150, 1307
CSO ₂ C asymmetric stretch	1322
C-O asymmetric stretch	1244, 1260-1000
C ₆ H ₆ ring stretch	1587-1489
O-H aliphatic and aromatic stretch	2886, 2938 and 2971

Table 4: FTIR spectra of pure DMAc.

DMAc. spectra	Wave number cm^{-1}
C = O stretch	1736, 1760-1670
C-N stretch	1340-1020

Table 5: FTIR spectra of pure MDEA

MDEA spectra	Wave number cm^{-1}
Amine C-N stretch	1340-1020
O-H stretch	3640-3160

Table 6: FTIR spectra of pure MEA

MEA spectra	Wave number cm^{-1}
C-N stretch	1340-1020
O-H stretch	3640-3160
N-H stretch	3500-3300

Table 7: FTIR spectra of pure DEA

DEA spectra	Wave number cm^{-1}
C-N stretch	1340-1020
N-H stretch	3500-3300
O-H stretch	3640-3160

Thus in this study a complete vibrational analysis is attempted and in the present study the FTIR spectra of the PVAc., PES, PSF and amines were recorded analysis was carried out. Using their results various modes of vibrations and their probable assignment have been discussed. The chemical structures of these chemicals are shown in Fig. 1 to 3 and spectra are shown in following Table 1 to 7.

EXPERIMENTAL

Materials: Polyethersulfone (PES) ULTRASON® E-6020 P was purchased from BASF Germany having a glass transition temperature (T_g) of 260°C. Polysulfone (PSF) Udel® P-1800 having a glass transition temperature (T_g) of 185°C was acquired from Solvay Advanced Polymers, L.L.C, U.S. PES was in the form of beads and PSF was in powdered form. Polyvinyl Acetate (PVAc.) average $M_w \sim 100,000$ by GPC, beads from Sigma Aldrich having a glass transition temperature (T_g) 30°C. Dimethyl Acetamide (DMAc.) solvent and methyl diethanol amine, mono ethanol amine, diethanol amine with a purity of 99.99% was purchased from Merck.

Fourier transform infrared spectroscopic study: In order to investigate the interaction between two polymers and amines FTIR analysis of developed blend membranes was exploited. The FTIR taken by Perkin Elmer Spectrum One FTIR Spectrometer. The scans are 20 and the wave length range is 4000-450 cm^{-1} and the spectra were obtained from a 200 μm diameter sampling area. The membrane samples were cut at random positions from casting films dried more than 48 h at room temperature and then clamped to the plate. All spectra were corrected for the FTIR characteristic progressive increase in the absorbance at lower wave numbers, using the equipment software.

RESULTS AND DISCUSSION

In, Graph 1 (Appendix) the FTIR of polymeric membrane of PVAc. Shows the following functional group C = O, C-O and C-H. In pure PVAc. Spectra the wave length of C = O is 1736.00 cm^{-1} and when the membrane is develop in DMAc. solvent, the peak is shifted to 1630.65 cm^{-1} due to the presence of amide group. In the carboxylic group the C-O, the peak is appears from 1244.00 to 1025.72 cm^{-1} due to hydrogen bonding (Ahmed *et al.*, 2011). The C-H group in Phenyl ring substitution bends of pure PVAc. is 850.00 cm^{-1} , the band is shifted towards 801.85 cm^{-1} due to asymmetric stretching in CH₃ (Morris, 1943; Jensen *et al.*, 1972).

In, Graph 2 (Appendix) the FTIR of polymeric membrane of PES in DMAc. Solvent have the following functional groups. The sulfone group S = O

asymmetric have the wave number 1150.00 cm^{-1} , the peak appears on 980.69 cm^{-1} due to benzene ring ortho, meta, para positions. The next functional group is CSO_2C asymmetric stretch is 1322.00 cm^{-1} , the peak is shifted to 1290.45 cm^{-1} due to stretching vibration of SO_2 group. The C-O group has wave number 1244.00 cm^{-1} and that is shifted to 1160.32 cm^{-1} due to hydrogen shifting bonding (Ahmed *et al.*, 2011). The C_6H_6 ring stretch has wave number 1587.00 cm^{-1} which is not shifted due to strong bonding or stable condition of aromatic ring. The OH aliphatic group the wave number is 2886 cm^{-1} , the peak is shifted to 2675.99 cm^{-1} due to weak electronegativity.

In, Graph 5 (Appendix) the FTIR of polymeric blend membrane of PVAc. 10% and PES 90% in DMAc. solvent the C = O has a wave number 1736 cm^{-1} but in the blend there is no far changes the peak and it is stable in 1725.46 cm^{-1} (Durgaprasad *et al.*, 1971; Anthoni *et al.*, 1974). The C-O stretch is on 1244 cm^{-1} in PES and PVAc., the peak is shifted to 975.78 cm^{-1} due to these spectral changes indicated the existence of molecular interaction in polymeric blend (Ahmed *et al.*, 2011). The Phenyl ring substitution bend C-H wave number is 850 cm^{-1} , the peak shift to 857.39 cm^{-1} , no change due to stable condition. The S = O symmetric and CSO_2C asymmetric stretch, wave number is 1150 and 1322 cm^{-1} , the peaks are shifted to 1095.23 and 1320.16 cm^{-1} respectively, due to stretching vibration mode. In this blend membrane the C_6H_6 and OH, the wave number of C_6H_6 the peak is not shifted and it is still present on 1587.27 cm^{-1} but in OH stretch group the peak is shifted to 2795.42 cm^{-1} due to weak electronegativity.

In, Graph 9 (Appendix) the FTIR of polymeric blend membrane of PVAc. 10%, PES 90% and MDEA amine 10% is blend in DMAc solvent, the Ketone group C = O stretch 1736 cm^{-1} have no big change and the peak is 1729.03 cm^{-1} . The carboxylic acid C-O in stretch region of PVAc. and PES, the peak is 1070.82 cm^{-1} due to hydrogen shifting bonding (Ahmed *et al.*, 2011). In C-H group peak has a change and it is on 756.96 cm^{-1} . The Sulfone symmetric group and CSO_2C asymmetric stretch, the peak is shifted to 940.08 and 1300.79 cm^{-1} respectively, due to benzene ring ortho, meta, para position. The benzene peak appears on 1530.89 cm^{-1} and OH group peak appears on 2420.11 cm^{-1} due to weak electro negativity of hydroxyl group. The spectral change was observed for C-N amine, to 840.62 cm^{-1} due to replacement of hydrogen bonding. The OH group the wave number is 3640 cm^{-1} band is shifted in stretch region 3582.54 cm^{-1} because of weak electro negativity of hydroxyl group.

In, Graph 10 (Appendix) the FTIR of polymeric blend membrane of PVAc. 10%, PES 90% and MEA amine 10%, the C = O stretch 1736 cm^{-1} , peak is not change due to bonding in stable condition. The Carboxylic group peak turns to 1200.00 cm^{-1} due hydrogen bonding in PVAc. and PES. The CH stretch of Phenyl ring substitution band, the peak remains on

850.20 cm^{-1} . The Sulfone S = O symmetric stretch is shifted to 1128.36 cm^{-1} and CSO_2C asymmetric stretch, the peak is on 1276.16 cm^{-1} band due to stretching vibration. The C_6H_6 peak also not shifted and has the wave length 1587.25 cm^{-1} . The OH Aliphatic peak also has not changed and still on 2886.19 cm^{-1} . The C-N amine stretch 1020 cm^{-1} is shifted to 950.42 cm^{-1} due to weak hydrogen bonding. The amine N-H stretch peak remains in original position 3400.15 cm^{-1} . The OH group in MEA, peak is also remaining in original position that is 3640.88 cm^{-1} , as mentioned in Table 7.

In, Graph 11 (Appendix) the FTIR of polymeric blend membrane of PVAc. 10%, PES 90 and 10% amine, the C = O Ketone group peak is not shifted and it retain on its original position. The Carboxylic acid C-O stretch in PVAc and PES, the peak is shifted to 1050.77 cm^{-1} due to hydrogen bonding (Ahmed *et al.*, 2011). The C-H Phenyl ring substitution band, there is no big change occur and it is stable at 825.94 cm^{-1} . The Sulfone S = O symmetric and CSO_2C asymmetric stretch, the band is shifted to 950.30 and 1265.89 cm^{-1} respectively. The Benzene C_6H_6 and OH Aliphatic there is no change in benzene but OH peak is shifted to 2520.46 cm^{-1} due to weak electro negativity of hydroxyl ion. The C-N amines stretch, the band appears at 870.59 m^{-1} and N-H band is shifted to 3140.20 cm^{-1} due to vibration stretch.

In, Graph 3, 4, 6, 7 and 8 (Appendix) the Sulfone group S = O symmetric in polysulfone the wave number is 1150.00 cm^{-1} , the peak is shifted to 995.89 , 1150.11 , 1100.78 , 1150.13 and 1100.35 cm^{-1} , respectively there is no big change occur due to vibration stretching. The CSO_2C asymmetric stretch the peak is slightly shifted 1323.53 , 1310.26 , 1230.61 , 1322.79 and 1280.17 cm^{-1} respectively, due e to hydrogen bonding. The C-O asymmetric stretch in PSU and PVAc the wave number is 1244 cm^{-1} , the peak is shifted to 1018.45 , 1060.54 , 1020.43 , 1205.99 , 1180.27 cm^{-1} , respectively due to hydrogen shifting bonding (Ahmed *et al.*, 2011). The C_6H_6 ring stretch the wave number is 1587.00 cm^{-1} and the peak is on 1579.33 , 1580.67 , 1580.53 , 1581.23 and 1580.00 cm^{-1} respectively, there is a slightly change in these peaks and remain stable. The OH Aliphatic stretch the wave number is 2886.00 cm^{-1} , band occurs on 2880.15 , 2860.44 , 2680.83 , 2880.11 and 2730.51 cm^{-1} respectively, due to weak electro negativity of OH negative ion.

In, Graph 4, 6, 7 and 8 (Appendix) the C = O Ketone in PVAc. the peak is shifted to 1730.37 , 1730.92 , 1736.61 and 1732.82 cm^{-1} respectively, no change occur in structure bonding but slightly vibration due to stretching. The C-H Phenyl ring substitution band wave number is 850 m^{-1} , the peak is shifted towards 842.23 , 830.66 , 833.84 and 848.39 cm^{-1} respectively, the peak is slightly change from original position but it comes in range due to stable hydrogen bonding.

In, Graph 6 to 8 (Appendix) the amines C-N stretch wave number is 1020.00 cm^{-1} , the peak is turn towards 914.24 , 1015.55 and 985.73 cm^{-1} respectively, the change occur in the peak due to hydrogen bonding. In OH stretch wave number is 3640.00 cm^{-1} , the peak is shifted to 3616.69 , 3455.27 and 3639.46 cm^{-1} respectively, the change is occurring by the hydroxyl ion.

In, Graph 7 and 8 (Appendix) the N-H group is present in MEA and DEA amine. The wave number is 3400.00 cm^{-1} , the peak is 3060.09 and 2462.99 cm^{-1} respectively, due to weak hydrogen bonding with N atom.

CONCLUSION

The present research addresses the current needs of having high permeability and selectivity membrane for removal of CO_2 from natural gas. The developed polymeric 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. In the present study PSU/PES/PVAc. Blend with amines MEA, MDEA and DEA flat sheet dense membranes are prepared by solution casting and evaporation method. From FTIR analysis the miscibility of polymeric blends is confirmed because a

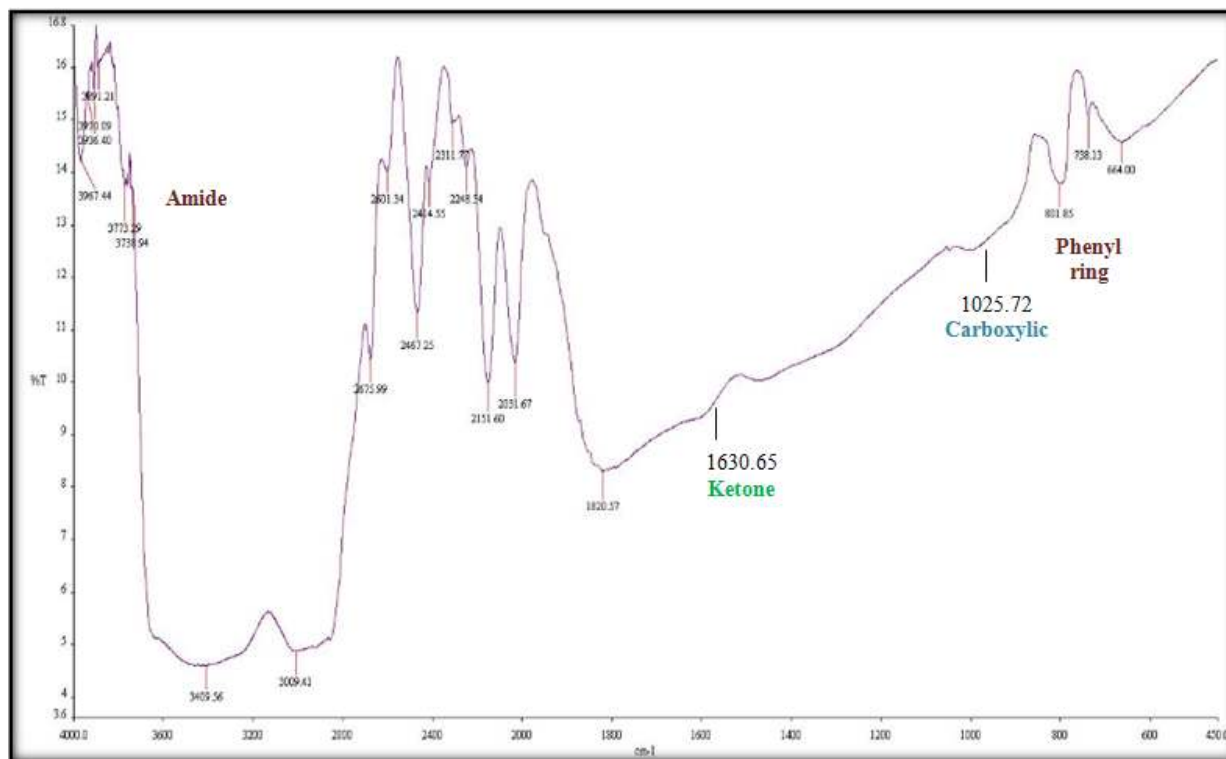
few shifts are seen in FTIR spectra. Furthermore there is no cross linking or formation of intermediates. FTIR analysis of this blended membrane showed that the frequency was shifted for the characteristic peaks involving di-aryl sulfone, ether, C = O, C-O groups of PSU/PES/PVAc. along with the C-N, N-H group of amines. These spectral changes indicated the existence of molecular interaction among the polymeric blends; highlight the compatible nature among each other.

In the future study we also add the inorganic fillers like carbon molecular sieves; zeolites in blend which is further enhanced the polymeric blend membrane. Therefore, this can increase the economic process in gas trade.

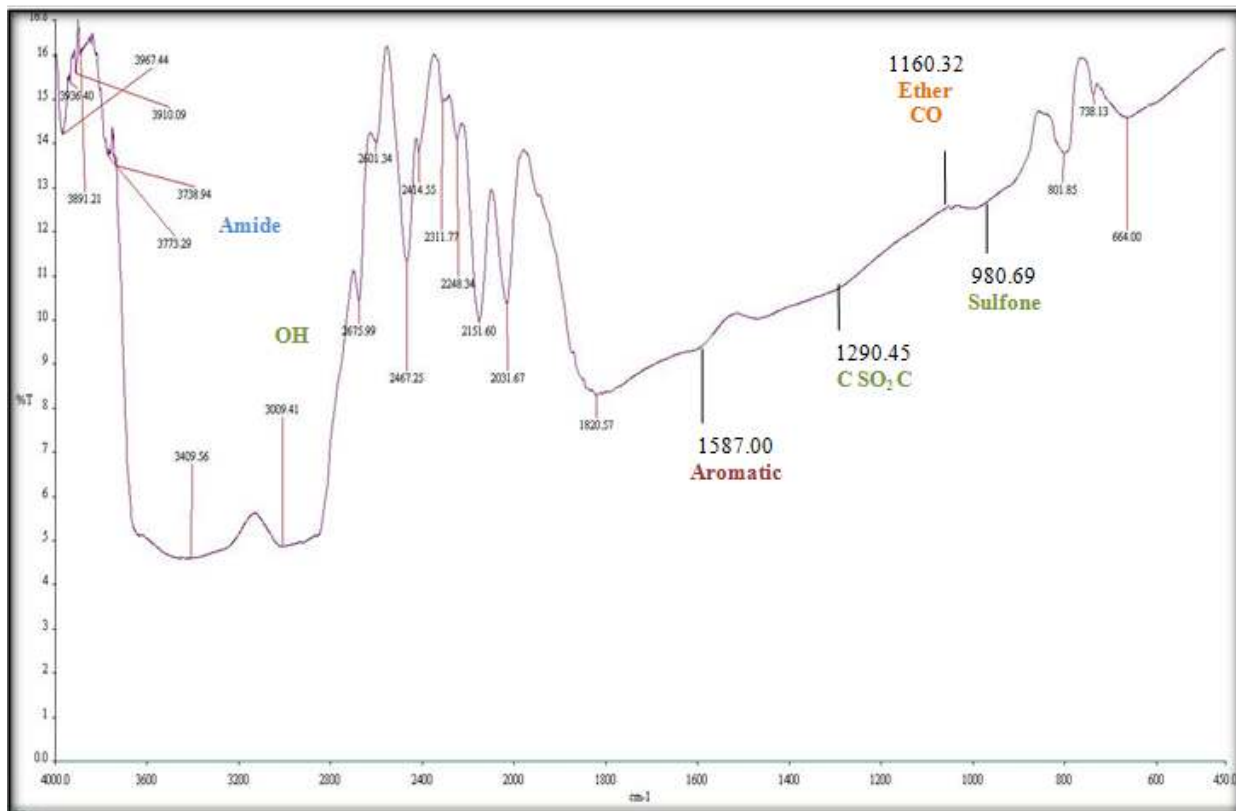
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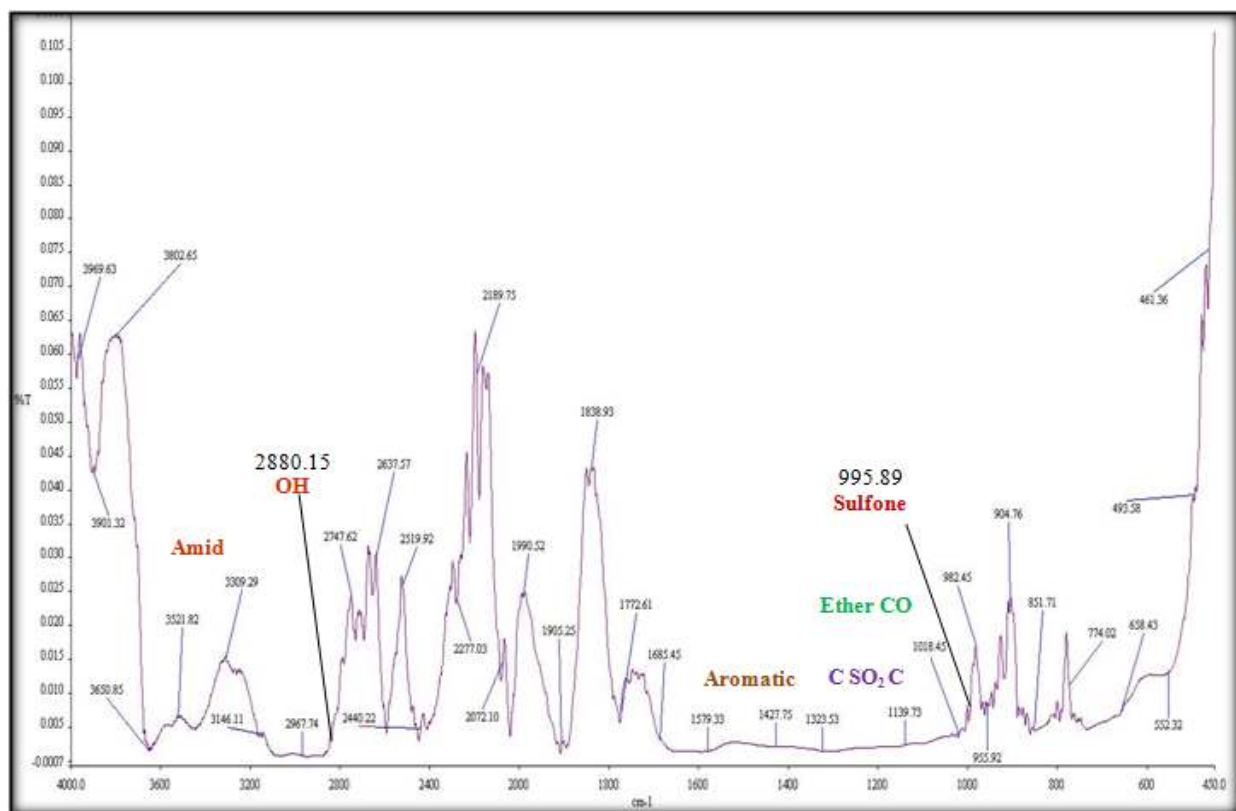
APPENDIX



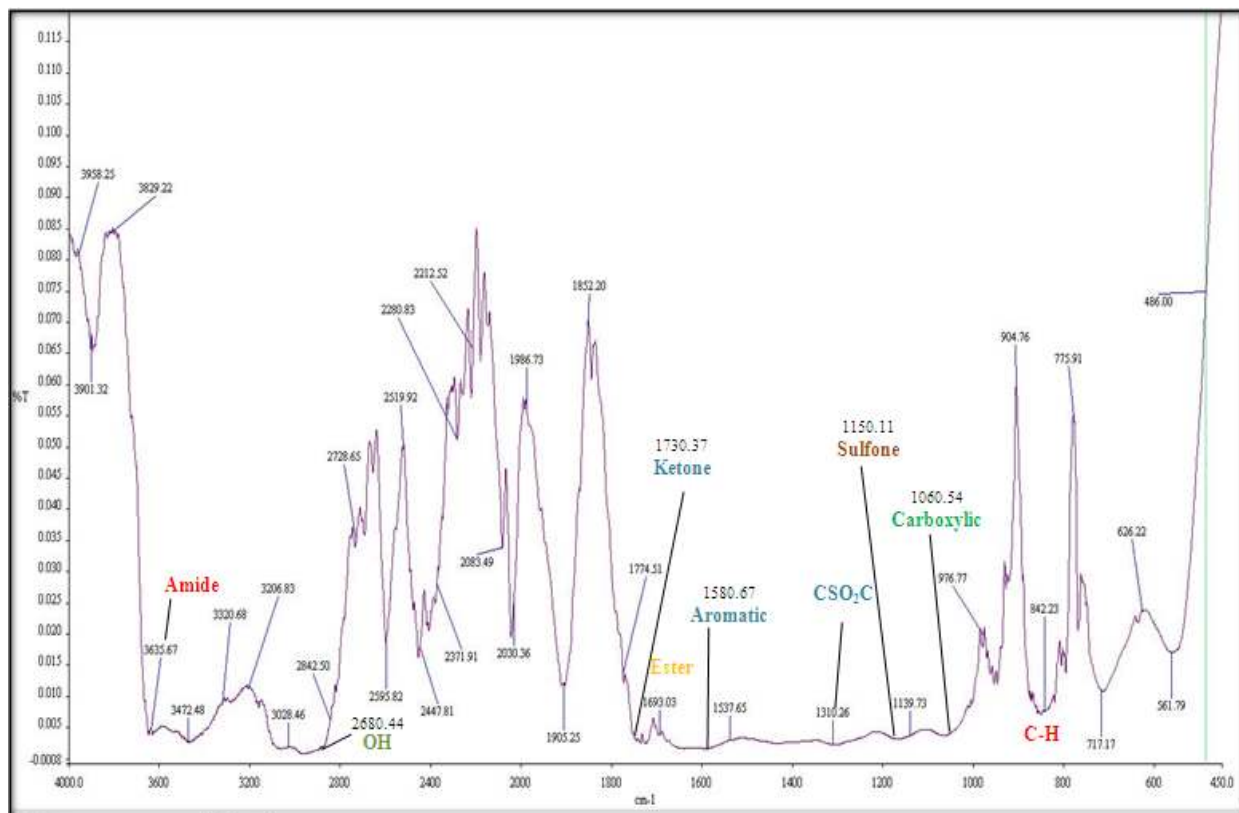
Graph 1: FTIR of polymeric membrane of PVAc



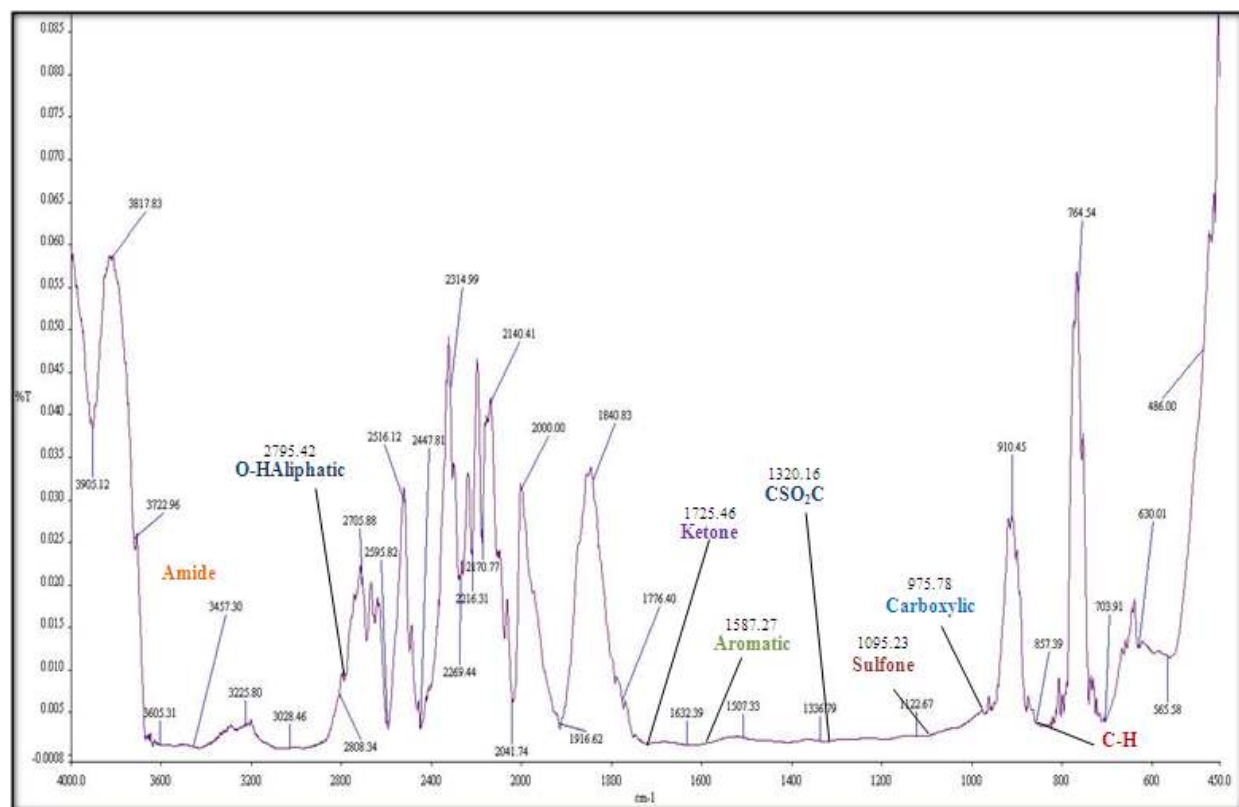
Graph 2: FTIR of polymeric membrane of PES



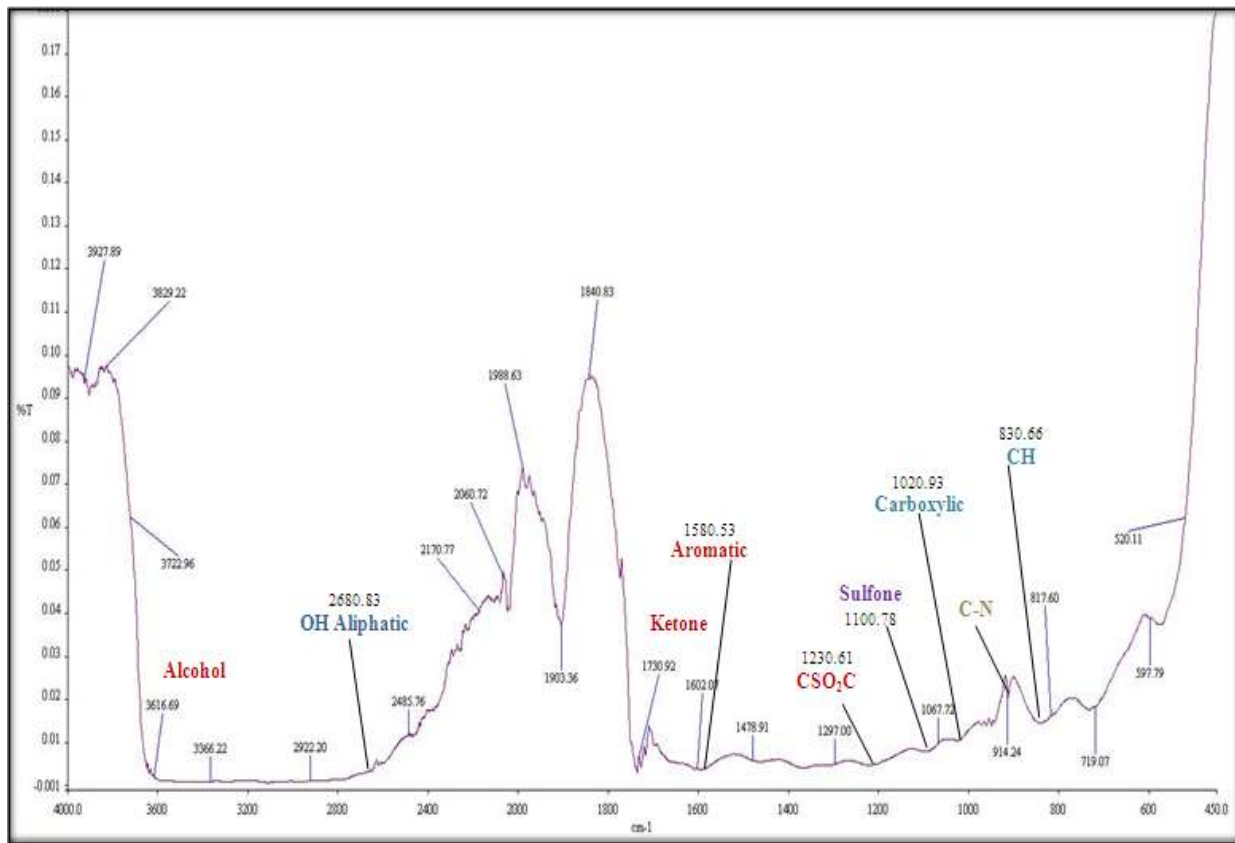
Graph 3: FTIR of polymeric membrane of PSU



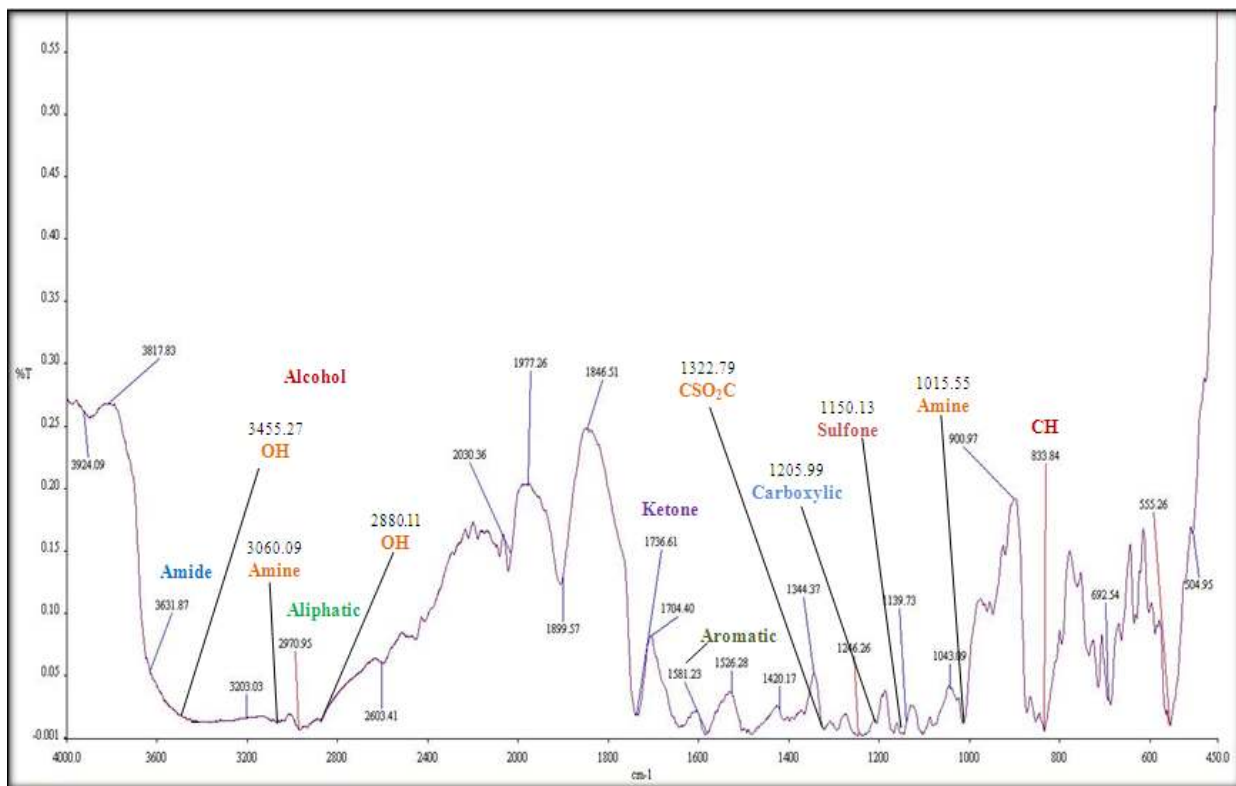
Graph 4: FTIR of polymeric blend membrane of PVAc. (10%) and PSU (90%)



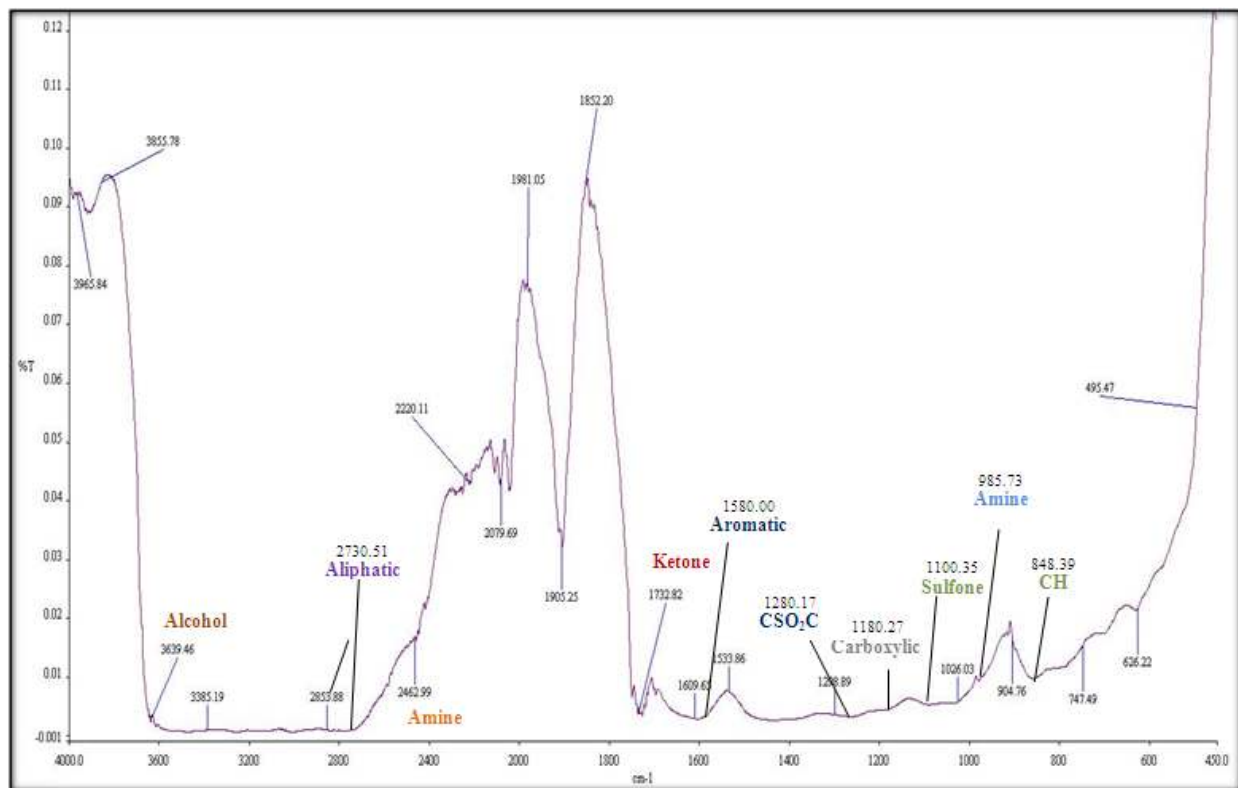
Graph 5: FTIR of polymeric blend membrane of PVAc. (10%) and PES (90%)



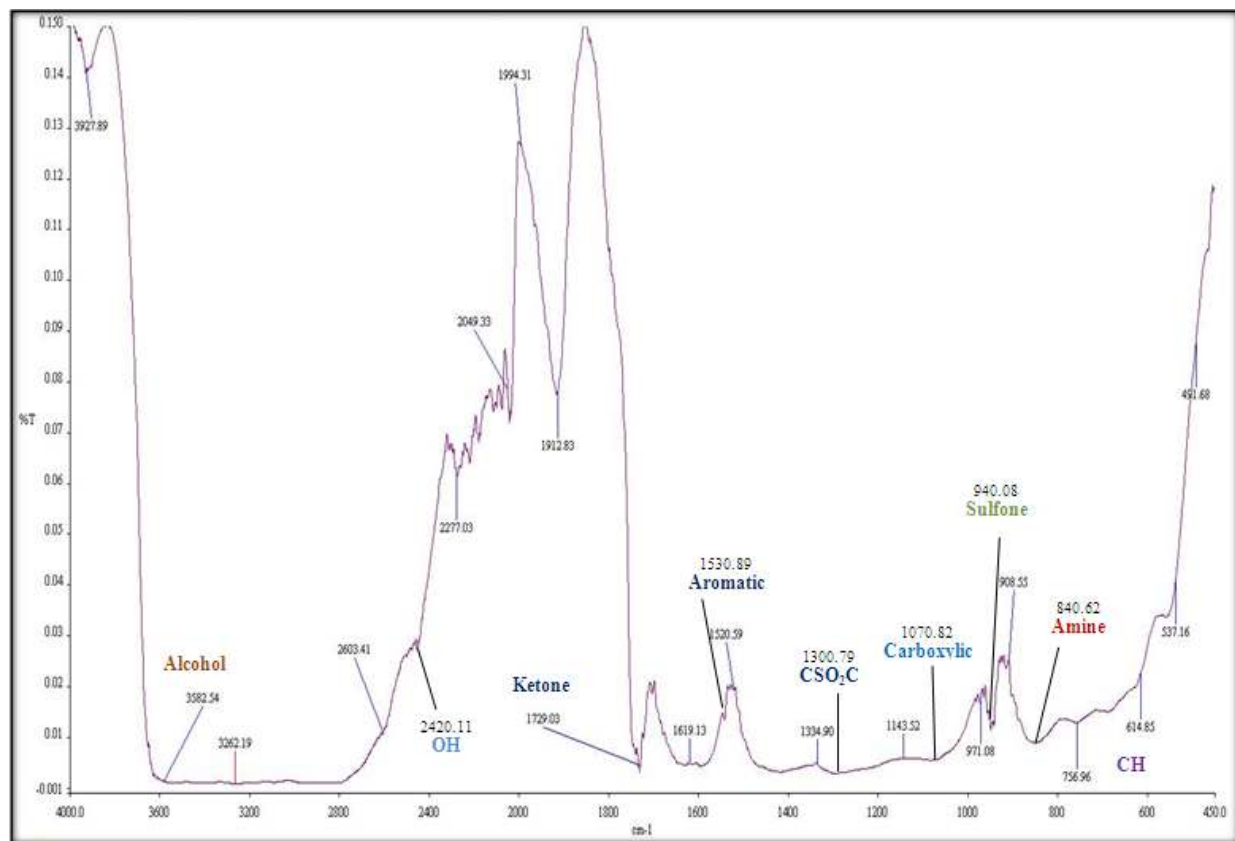
Graph 6: FTIR of polymeric blend membrane of PVAc. (10%), PSU (90%) and MDEA (10%)



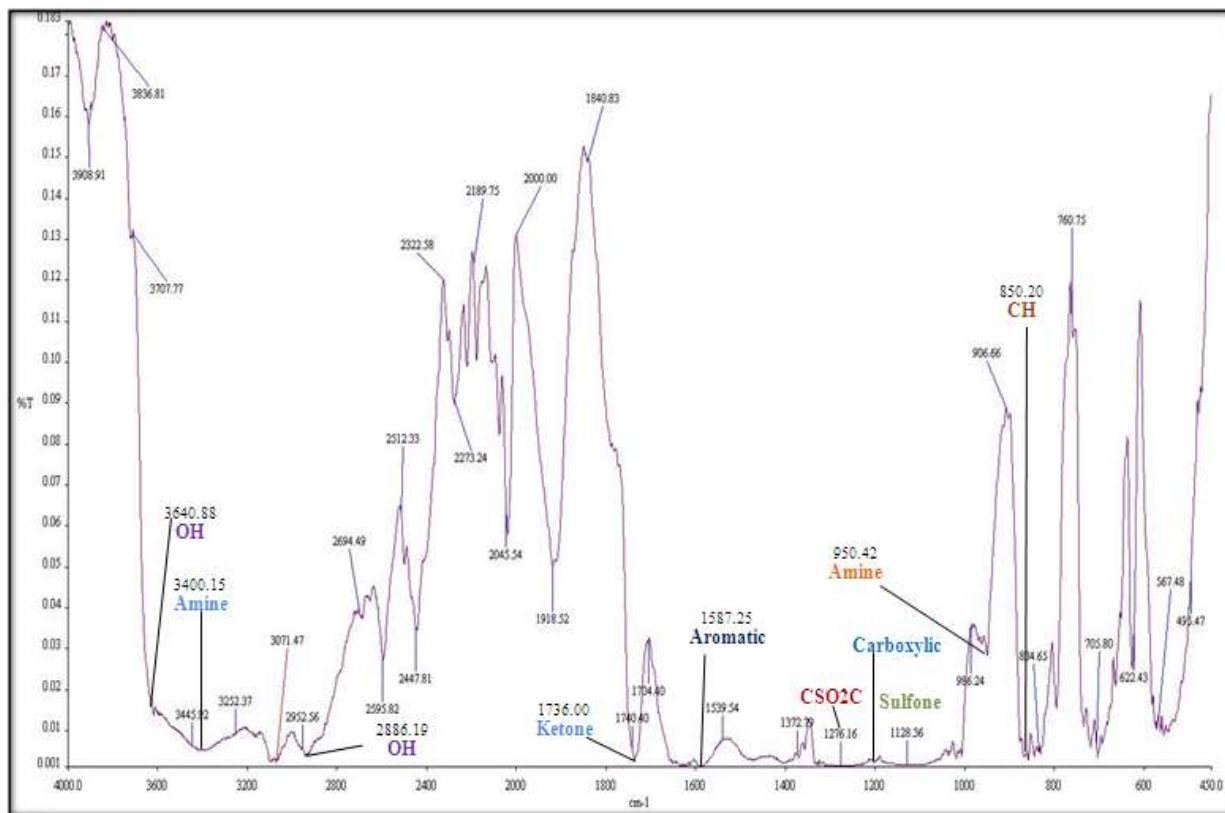
Graph 7: FTIR of polymeric blend membrane of PVAc. (10%), PSU (90%) and MEA (10%)



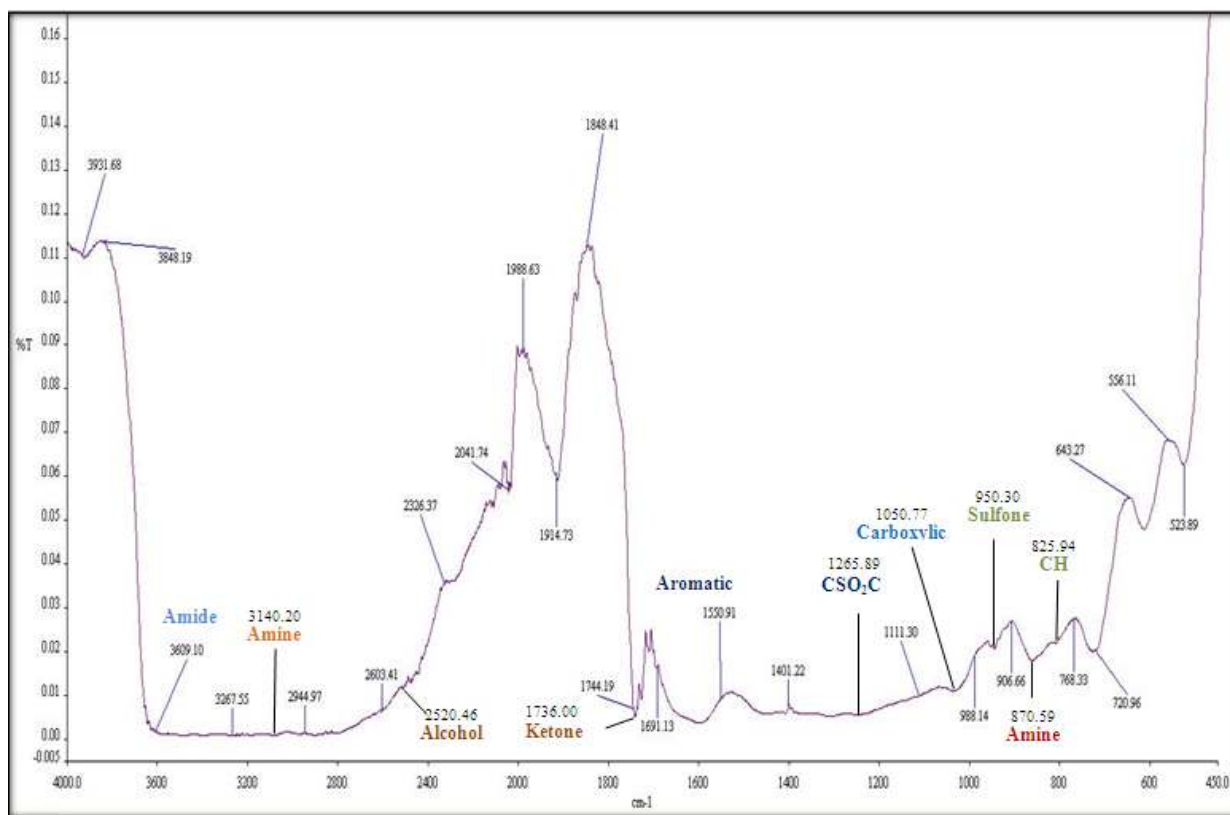
Graph 8: FTIR of polymeric blend membrane of PVAc. (10%), PSU (90%) and DEA (10%)



Graph 9: FTIR of polymeric blend membrane of PVAc. (10%), PES (90%) and MDEA (10%)



Graph 10: FTIR of polymeric blend membrane of PVAc. (10%), PES (90%) and MEA (10%)



Graph 11: FTIR of polymeric blend membrane of PVAc. (10%), PES (90%) and DEA (10%)

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