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Fabrication, Characterization and Performance Study of N-methyl-diethanolamine (MDEA)-Polyethersulfone (PES) Amine Polymeric Membrane for CO_2/CH_4 Separation

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Abstract: The polymeric membrane is a well-known membrane due to ease of processing and mechanical stability. These membranes extensively used for the separation of carbon dioxide from methane but the applications of these membranes are limited in order to achieve high permeability and selectivity. In this study the amine polymeric membrane has been fabricated by the addition of N-methyl-diethanolamine in polyethersulfone solution, the N- methyl-2 pyrrolidone used as solvent. The characterization of fabricated membrane has been carried out in order to investigate the morphology, thermal properties and identification of functional group by using field emission scanning electron microscope, thermo gravimetric analyzer and fourier transform infrared spectroscopy. The permeability and selectivity study were also carried out by using pure carbon dioxide and methane. The permeability and selectivity has been increased as compared to pure polyethersulfone membrane.

Key words: Amine polymeric membrane, characterization, CO_2 separation, permeability, selectivity

INTRODUCTION

Membrane technology is playing an important role in the gas separation. The low energy requirements and compact process design made this technology environmentally and economically beneficial as compared to other separation processes (Bernardo *et al.*, 2009).

The pressure difference across the membrane is a key parameter for the separation of gases thorough membrane (Mulder, 1996). Gas separation membranes have been used extensively for various applications H_2/N_2, H_2/CH_4, He/N_2, O_2/N_2 and CO_2/CH_4. The removal of CO_2 from methane CH_4 is the major application in natural gas processing (Baker, 2009).

Polymeric membrane materials have been used for various applications due to their relatively low initial costs and their capacity (Yampolskii, 2012). Although, there are some limitations such as low gas separation performance, poor chemical and thermal stability and plasticization, their ability to employ in gas separation applications is still limited (Bernardo *et al.*, 2009).

Alkanolamines are widely used for the removal of CO_2 and H_2S from sour gas. In amine based purification Monoethanolamine (MEA), Diethanolamine (DEA), Methyldiethanolamine (MDEA), has been suggested as promising solvents for the removal of acid gases (Davis and Rochelle, 2009). The addition of these functional group (amines) in polymer matrix also helps for uniform distribution of particles (Nasir *et al.*, 2013). However, limited literature has been reported in order to identify the best amine according to application. The efficiency of most amine units are not high, but these units could be efficient by changing the amines (Polasek and Bullin, 1984).

This research has been carried out for the fabrication of amine polymeric membrane for CO_2/CH_4 separation. This membrane has the properties of amine solution and polymeric membrane.

MATERIALS AND METHODS

Polyethersulfone PES (ULTRASON E 6020P) was purchased from BASF Germany, its molecular weight is 50,000 g moL^{-1}. Polyethersulfone was a main polymer for the fabrication of polymeric membranes. N-Methyl-2-Pyrrolidone (NMP) was obtained from Merck Germany. NMP was used as solvent for the preparation of polymeric solution.

Methyldiethanolamine (MDEA) was purchased from Merck Germany. This amine was used for the synthesis of amine supported polymeric membrane.

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Synthesis of flat sheet amine polymeric membrane: The polymer (PES) was added in the solvent (NMP) with the weight ratio of 20 wt%. The addition of polymer in the solvent was carried out at room temperature with continuous stirring. After the complete mixing of polymer then added different concentration (5, 10 and 15 wt%) of MDEA and let the solution on stirring for 24 h. The viscous dope solution was prepared after 24 h. The solution kept for another 24 h at room temperature for stabilization. Then casted the dope solution on the glass plate by using casting machine, by adjusting the knife angle to 180 microns. Then put the membrane in oven at 90°C for next 24 h.

Characterization of amine polymeric membrane: The characterization of newly developed membrane was carried out in order to identify the functional groups, find the membrane morphology and determine weight loss. FTIR, FESEM and TGA were the equipments for the characterization of membranes.

Gas permeability study: The developed membranes were tested for a pure carbon dioxide (CO_2) and methane (CH_4) gases using variable pressure of 2, 4, 6, 8 and 10 bars. The permeance was measured after the steady state was reached, which took about 10-15 min.

RESULTS AND DISCUSSIONS

Field Emission Scanning Electron Microscope (FESEM) analysis: The cross sectional view of the newly developed membrane has shown in Fig. 1. The new PES-MDEA membrane has dense structure. All amine concentrations formed homogenous compatible solution with PES polymer matrix.

Fourier Transforms Infrared Spectroscopy (FTIR) analysis: FTIR spectroscopy of pure PES, PES-MDEA (5%) membrane, PES-MDEA (10%) and PES-MDEA (15%) membranes was employed to identify interactions between the different components, with same compositions at the molecular level. In this analysis the sulfone group (SO_2) peak has been shown at 1145 cm^{-1}. The peak at 1202 cm^{-1} has been related to ether (C-O-C) and the aromatic benzene ring has been located at the 1480 and 1589 cm^{-1}. By the addition of 5 and 10% MDEA

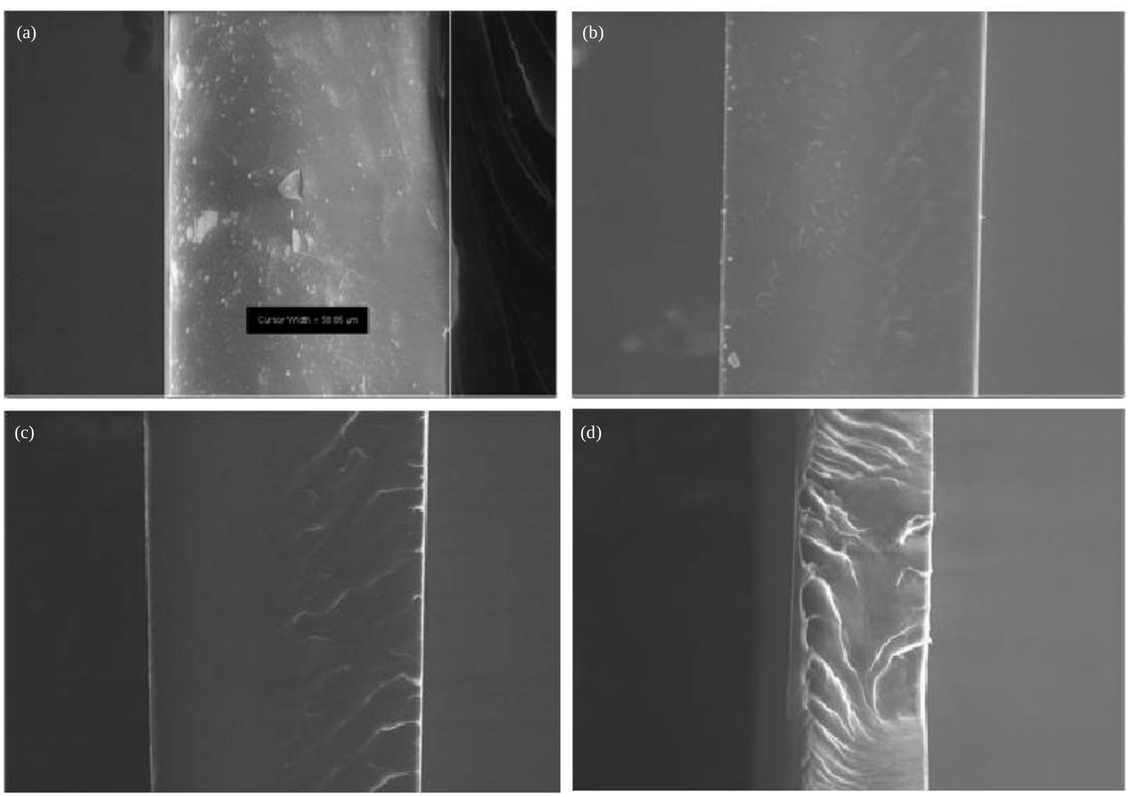

Fig. 1(a-d): FESEM analysis (a) Pure PES membrane, (b) 5% PES-MDEA membrane, (c) 10% PES-MDEA membrane and (d) 15% PES-MDEA membrane (magnification 5000X)

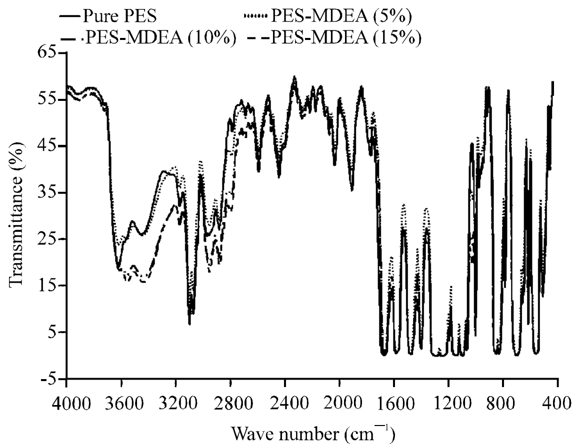

Fig. 2: FTIR analysis of PES-MDEA polymeric membrane

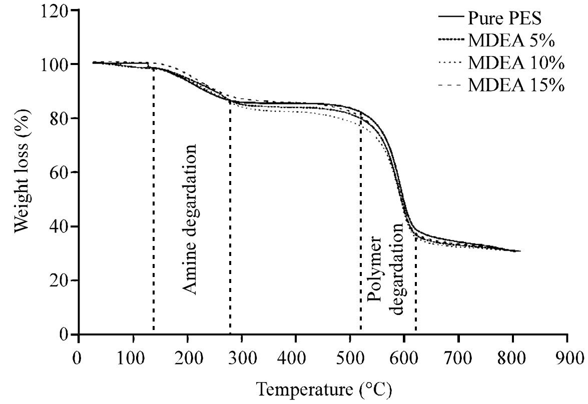

Fig. 3: TGA analysis of PES-MDEA amine polymeric membrane

the wave number for sulfone has been shifted to 1144 and 1146 cm^{-1} for 15% MDEA addition. The MDEA addition has been also changed the wave number of ether linkage to 1256 cm^{-1} for 5 and 10% MDEA and 1261 cm^{-1} for 15% MDEA. Slight shifting of aromatic benzene ring has been observed. The wave number for aromatic benzene ring has been shifted to 1480 cm^{-1} and 1587 cm^{-1} for 5 and 10% MDEA and 1479 and 1587 cm^{-1} for 10% MDEA. Due to formation of hydrogen bonding is the reason of this peak shifting (Fig. 2).

Thermo Gravimetric Analysis (TGA): The thermal decomposition behavior of the pure polyethersulfone (PES), PES-MDEA (5%), PES-MDEA (10%) and PES-MDEA (15%) polymeric membrane was studied by TGA. Figure 3 showed the weight loss of these membranes as a function of temperature. The heating range of sample was 30-800°C at the rate of 10°C min^{-1}. The Fig. 3 has been shown the two prominent curves, approximately between 150-300°C and 500-620°C. First curve has been shown the degradation of amine and second curve showed the degradation of polymer. By the addition of different concentration of amine the degradation temperature of polymer has been reduced may due to amine linkage with polymer or may be due to ether bond breakage. The Fig. 3 also showed that the weight loss of the polymer has been increased by the addition of amine. So, from this analysis the amine are present in the membrane.

Permeability studies: The gas permeability study has been carried out by using the pure CO_2 and CH_4 gases. By the addition of amine in the polymeric membrane the permeance of CO_2 has been increase as compared to pure PES membrane. In Fig. 4 the permeance of CO_2 has been decreased with increase in pressure, this is true behavior of glassy polymers. By the increase of amine concentration the permeance of CO_2 increasing as compared to pure PES membrane. The PES-MDEA (10%) membrane achieved high permeance as compared to PES-MDEA (5%) and PES-MDEA (15%) membrane. At 10 bars pressure all membrane experienced the increase in permeance. This phenomenon is normally known as plasticization.

Increase in permeance is due to the high CO_2 concentration in polymer matrix with disturbs the chain packing. This disturbance causes the increase in free volume of the polymer matrix. When the free volume has been increased the segmental mobility has been also increase. That's why the permeance increases with increase in pressure.

Permeance of CH_4 has been shown in Fig. 5. It has been observed that the permeance of CH_4 is less than CO_2 permeance, it shown that the membrane has the ability to remove the CO_2 from CO_2/CH_4 mixture. It also has been observed that by the addition MDEA, CH_4 permeance has been shown the increasing trend w.r.t., pressure. Iqbal *et al.* (2008) explained that the increase in CH_4 permeance shown that the membrane have some defect like pinholes. Khulbe *et al.* (1997) concluded another reason of this, if the solvent is present in the membrane then permeance will increase and selectivity will be decrease.

The effect of amine addition on selectivity has been shown in the Fig. 6. It observed that the selectivity increased in PES-MDEA (10, 15%) membranes as

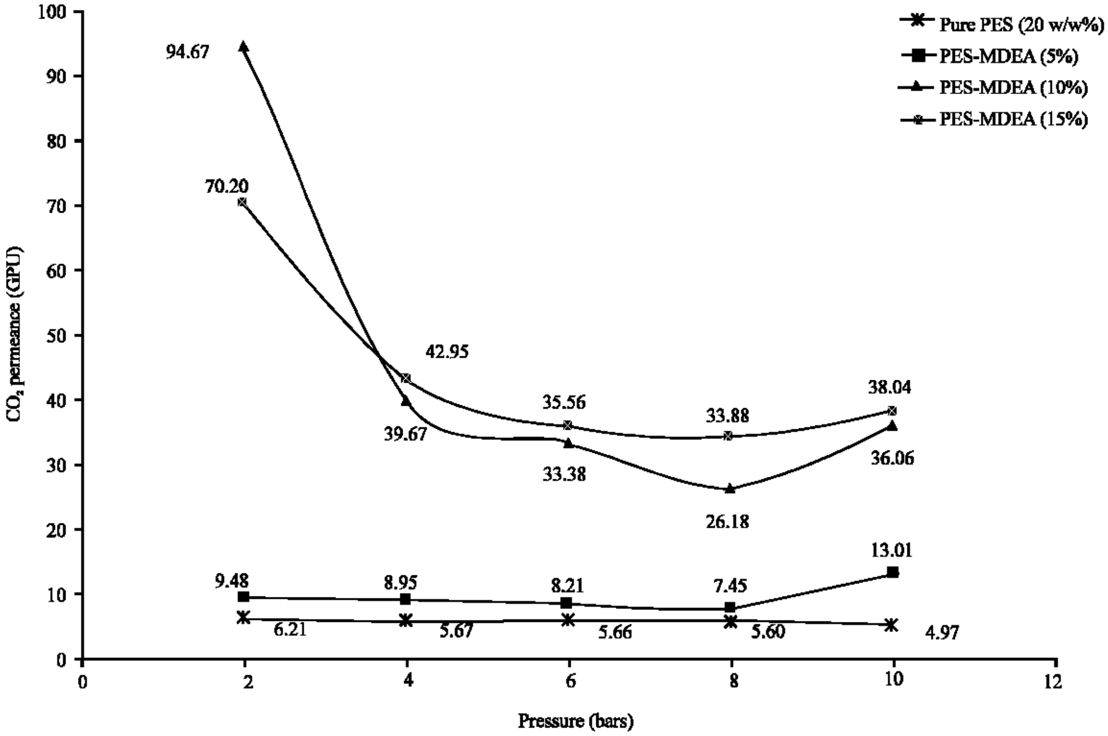

Fig. 4: CO_2 permeance across pressure

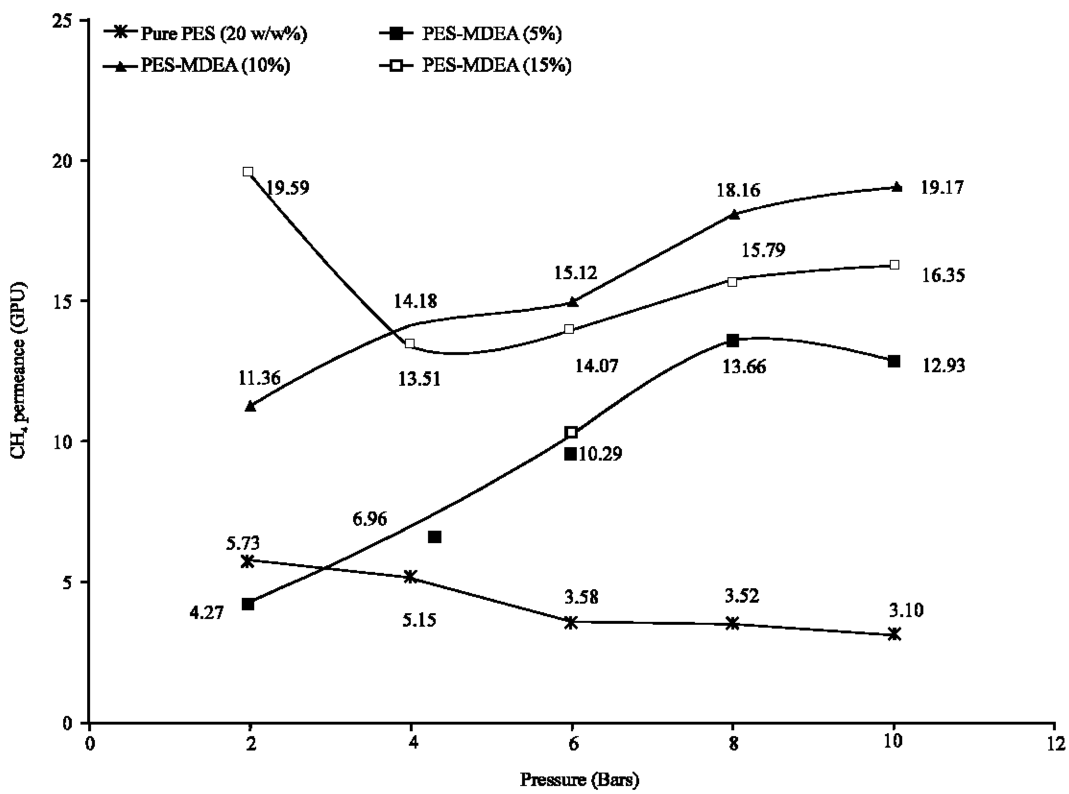

Fig. 5: CH_4 permeance across pressure

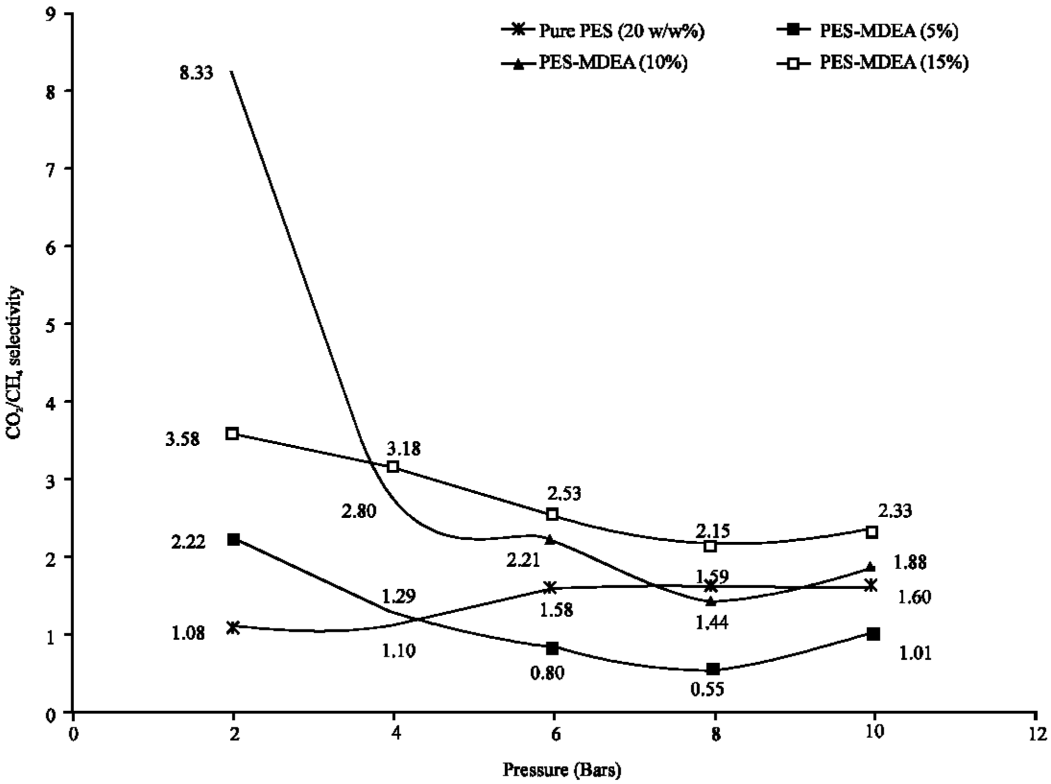

Fig. 6: CO_2/CH_4 selectivity across pressure

compared to pure PES membrane. The PES-MDEA (5%) membrane did not show any remarkable increase in the selectivity as compared to PES membrane. Figure 6 showed that the selectivity decreased by the increase of pressure. This shows the glassy behavior of membrane.

CONCLUSION

The amine polymeric membranes were fabricated by using MDEA as amine with different concentrations to check the effect of amine concentration on separation performance of PES polymeric membrane. It has been found that PES-MDEA (5%), PES-MDEA (10%) and PES-MDEA (15%) membranes has ability to separate more carbon dioxide as compared to pure PES membrane. The selectivity also increased in PES-MDEA (10%) and PES-MDEA (15%) membranes. It has been concluded that by the addition of amine permeance and selectivity of PES polymeric membrane can improve. Further studies are going on to improve the performance of amine polymeric membrane.

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