



## SYNTHESIS AND CHARACTERIZATION OF EDA-FUNCTIONALIZED POLYETHERSULFONE/SAPO-34 MIXED MATRIX MEMBRANE

N. N. R. Ahmad, H. Mukhtar, Z. Man and D. F. Mohshim

Department of Chemical Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar, Tronoh, Perak, Malaysia

E-Mail: [hilmi\\_mukhtar@petronas.com.my](mailto:hilmi_mukhtar@petronas.com.my)

### ABSTRACT

Modification techniques of the inorganic fillers have been introduced in the synthesis of mixed matrix membrane (MMM) in order to make the fillers become more compatible and homogeneously dispersed in the polymer matrix. It is also believed that enhancement in polymer/filler interaction can enhance the gas separation performance. In this work, SAPO-34 zeolite was functionalized using an organic amino cation, ethylenediamine (EDA) prior to embedment in the PES polymer matrix. The obtained PES/SAPO-34 mixed matrix membranes were characterized using Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric (TGA) and Field Emission Scanning Electron Microscope (FESEM) analyses in order to compare the properties between unmodified and modified MMM. It was found from FTIR analysis that EDA was successfully grafted onto the SAPO-34 surface. TGA analysis also showed that functionalized MMM exhibited an increase in membrane thermal stability. The use of EDA-functionalized SAPO-34 in the PES based MMM has improved the contact between polymer and filler interphase as revealed by FESEM images. This finding suggests that the functionalization technique using EDA can be used in the fabrication of MMM in order to enhance the compatibility between the polymer and zeolite.

**Keywords:** mixed matrix membrane, functionalized SAPO-34, CO<sub>2</sub>/CH<sub>4</sub> gas separation, organic amino cation.

### INTRODUCTION

Membrane development for the natural gas processing specifically for CO<sub>2</sub> gas removal has been one of the major concerns in the industrial gas separation applications. Membrane technology is attractive due to low capital investment, simplicity and high product recovery (Mannan *et al.* 2013; Shimekit and Mukhtar, 2012). Mixed matrix membrane (MMM) consists of inorganic fillers dispersed in polymer matrix which act as a continuous phase. This type of membrane combines superior properties of each phase i.e.; high selectivity of the inorganic fillers and desirable mechanical properties and economical processability of polymer (Vu, Koros and Miller, 2003; Moore, Mahajan and Koros, 2004; Nasir *et al.* 2013).

One of the challenges in the fabrication of MMM is related to the poor contact between the rigid glassy polymer and the inorganic surface. This results in the formation of undesirable voids around the fillers and could reduce the gas selectivity. Various modification techniques have been applied in the fabrication of MMM in order to improve the compatibility between the fillers and polymer and hence, enhance the gas separation efficiency. Some researchers used the approach of grafting the zeolite's surface with silane coupling agent (Junaidi *et al.* 2014a; Li *et al.* 2006). They found that the CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity for the modified MMM are higher compared to unmodified MMM. Mohshim *et al.* (2014a) added the ionic liquid as the third component in MMM formulation which can act as the wetting agent around the filler and improve the polymer/filler interaction. Rafizah and Ismail (2008) reported on the modification of MMM by treating the carbon molecular sieve (CMS) with a sizing agent prior to embedment into the polymer matrix. Inclusion of low molecular weight additives such as 2-

hydroxy 5-methyl-aniline (HMA) into MMM can also improve the interphase interaction and increase the gas selectivity (Cakal, Yilmaz and Kalipcilar, 2012)

Numerous attentions have been given to zeolites as inorganic fillers in the fabrication of MMM due to their excellent transport properties (Goh *et al.* 2011; Junaidi *et al.* 2014b). SAPO-34 which belongs to the zeolite group is promising for the CO<sub>2</sub>/CH<sub>4</sub> gas separation application since its pore size (0.38nm) is larger than CO<sub>2</sub> gas kinetic diameter (0.33nm) and similar with CH<sub>4</sub> kinetic diameter (0.38 nm) (Yeo, *et al.* 2012). In this work, SAPO-34 was used as the fillers in the polyethersulfone (PES)-based mixed matrix membrane. This zeolite was functionalized with organic amino cation i.e. ethylenediamine (EDA) in order to enhance the selective CO<sub>2</sub> adsorption and improve the filler/polymer compatibility. The selection of EDA as the functionalizing agent in this work was based on the report of Venna and Carreon who observed the excellent CO<sub>2</sub> capture of EDA-functionalized zeolite material (Venna and Carreon, 2011). To the best of our knowledge, no works on the modification of the PES based mixed matrix membrane using EDA have been reported so far. Modified PES/SAPO-34 MMM was fabricated and characterized in order to compare its properties with the unmodified MMM.

### METHODOLOGY

#### Materials

Polyethersulfone (Ultrason®E) (PES) was purchased from BASF SE, Germany. The polymers were dried at 120 °C overnight before dope preparation. N-methyl-pyrrolidinone (NMP) was Merck analytical grade and being used as a solvent due to its low toxicity. The SAPO-34 zeolite was purchased from ACS Material with



particles size in the range of 2-15  $\mu\text{m}$ . This zeolite was degassed at 150  $^{\circ}\text{C}$  for 24 hours before use. Materials for SAPO-34 modification include; EDA was Merck analytical grade, toluene was purchased from R&M and ethanol (99% purity) was obtained from Hmbg.

### Functionalization of SAPO-34 zeolite

The SAPO-34 zeolites were functionalized with organic amino cation based on the reference of Venna and Carreon (2011) and in this work, some modifications were applied in the functionalization methodology. About 50ml of toluene was mixed with 0.15mmol EDA and stirred homogeneously in a round bottom flask. Then, 0.5g zeolite was added to the solution and the mixture was functionalized under reflux for 6 hours at 105  $^{\circ}\text{C}$ . The product was filtered and washed with toluene and ethanol. The obtained functionalized zeolite was dried at 80  $^{\circ}\text{C}$  for 12 hours under vacuum.

### Synthesis of PES membrane and PES/SAPO-34 MMM

Firstly, zeolite was added to the NMP solution and stirred for 1 hr. The suspension concentration was about 20 wt% of zeolite (based on polymer weight basis). Then, approximately 10 wt% of total PES polymer was added to the zeolite suspension as a "priming step" and stirred for 2 hours. The remaining amount of polymer was added gradually and stirred for 24 hours in order to obtain a homogenous dope solution. The obtained solution was degassed under vacuum for 30 min in order to remove trapped bubbles. For membrane casting step, the solution was poured onto a clean glass plate and cast into a layer by using a casting machine knife with gap adjusted at 90 $\mu\text{m}$ . The cast membranes were dried under vacuum at 90  $^{\circ}\text{C}$  for 8 hours and continued to dry at 160  $^{\circ}\text{C}$  for 24 hours. After drying, the membranes were allowed to cool naturally to room temperature and stored for further characterizations.

### Characterization of SAPO-34 particles and mixed matrix membrane

Fourier Transform Infrared (FTIR) spectroscopy (Nicolet iS10) was used to analyze the functionalized SAPO-34 particles in order to confirm the incorporation of amino groups. The IR spectra were obtained with averaged over 32 scans. Thermogravimetric analysis using TGA equipment (STA 6000, PerkinElmer) was performed in order to investigate the weight loss in the samples associated with transition and thermal degradation. Samples of pure PES membrane and MMM were heated from 30 to 800  $^{\circ}\text{C}$  at the rate of 10  $^{\circ}\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. Field Emission Scanning Electron Microscope (FESEM) (Zeiss Supra55 VP) was used to observe the cross-section morphology of the pure membrane and mixed matrix membranes. Liquid nitrogen was used to fracture the membrane samples prior to scanning.

## RESULTS AND DISCUSSION

### Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Comparison between FTIR spectra of pure and EDA-functionalized SAPO-34 particles is shown in Figure-1. Both spectra show almost similar significant bands which represent typical characteristics of SAPO-34 crystals. The presence of O-H groups could be attributed to the broad absorption band in the region of 3568-3892  $\text{cm}^{-1}$ . Two peaks found at the frequency around 1629 $\text{cm}^{-1}$  and 1034  $\text{cm}^{-1}$  represent the H-O-H bend and T-O-T asymmetric stretching in the SAPO-34 respectively. Venna and Carreon (2011) also observed these peaks at almost similar frequencies. For functionalized SAPO-34 spectrum, a peak at 1390  $\text{cm}^{-1}$  which indicates the  $-\text{CH}_2\text{NH}_2$  group confirms the presence of amino functionalities in the zeolite (Socrates, 2004).

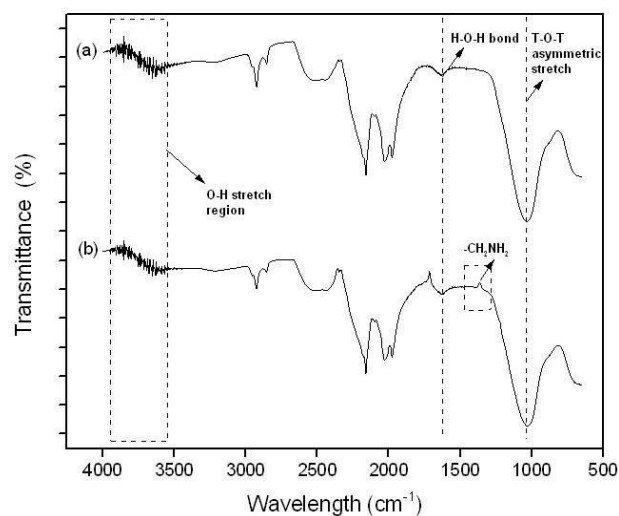


Figure-1. FTIR spectra of (a) pure SAPO-34 and (b) EDA-functionalized SAPO-34.

### Thermogravimetric analysis (TGA)

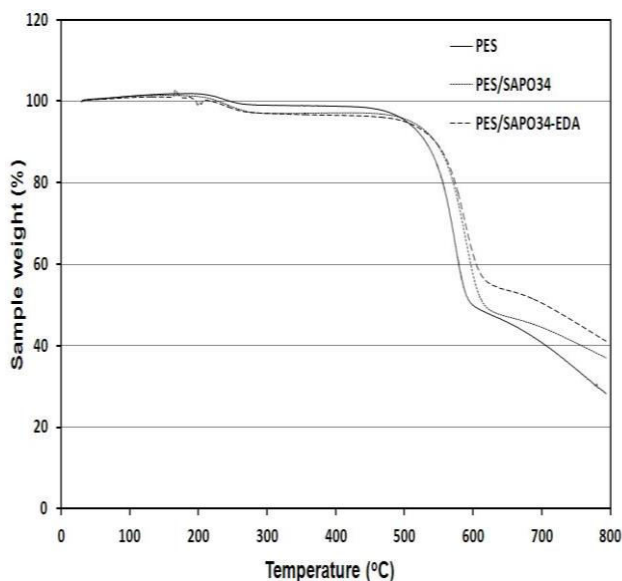
The amounts of weight loss for all membranes at different temperature range are tabulated in Table 1. The thermograms are illustrated as in Figure-2. It can be observed from Table 1 that pure PES membrane exhibited about 2.8% weight loss in the temperature range between 200 to 300  $^{\circ}\text{C}$  which could be assigned to the evaporation of NMP solvent in the membranes (Mohshim, Mukhtar and Man, 2014b). It is suggested that the drying time of membranes can be prolonged in order to reduce the amount of remaining solvent to a lesser extent. For MMM containing SAPO-34 particles, the weight losses around 200-300  $^{\circ}\text{C}$  were a little bit greater than that of PES membrane. This could be due to evaporation of solvent and impurities that might be trapped within the membranes containing SAPO-34 (Özgen, 2009). For pure PES membrane, a major weight loss (70 wt%) which started at the temperature around 430  $^{\circ}\text{C}$  could be attributed to the decomposition of PES polymer. It can be observed from Figure-2, the polymer decomposition



temperature in MMM started at a higher temperature which around 455 °C. The weight loss due to the polymer decomposition in PES/SAPO-34-EDA membrane at temperature 455-800 °C was also found to be lower than that of pure PES and PES/SAPO-34 membranes. This suggests that incorporation of EDA-functionalized SAPO-34 can increase the thermal stability of the MMM.

**Table-1.** Weight loss in membranes determine from TGA.

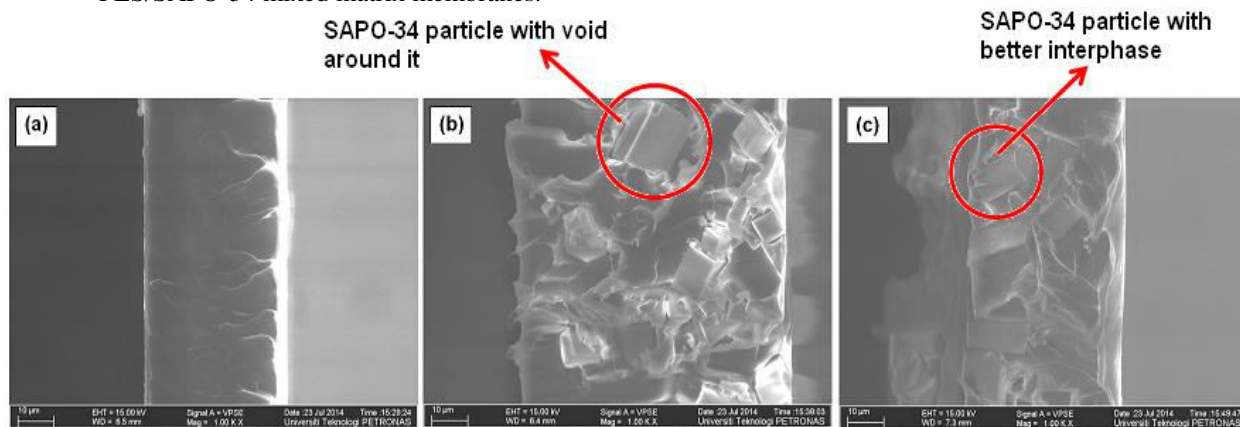
Temperature range (°C)	Weight loss (wt%)		
	PES	PES/SAPO-34	PES/SAPO-34-EDA
200-300	2.8	4.1	3.4
430-800	70.0	-	-
455-800	-	60.0	55.0



**Figure-2.** TGA curves for pure PES membrane and PES/SAPO-34 mixed matrix membranes.

### Field Emission Scanning Electron Microscopy (FESEM) analysis

Figure-3 shows the cross-section morphology of pure PES membrane and PES/SAPO-34 mixed matrix membranes. It can be observed from Figure-3(a), pure PES membrane shows a dense cross section structure. Mixed-matrix membrane, PES/SAPO-34 consists of a heterogeneous structure and some dark area around the SAPO-34 cubic particles could be attributed to the formation of voids. However, the MMM comprises of EDA-functionalized SAPO-34 shows more homogenous structure with no voids observed around the particles. This suggests that the grafting of the SAPO-34 with EDA has improved the contact at polymer/filler interphase. EDA grafted onto the zeolite surface contains amino functionalities that can interact with the polymer chain in the mixed matrix membrane and thus enhance the compatibility between these two phases.



**Figure-3.** Cross-section morphology of (a) pure PES membrane, (b) PES/SAPO-34 and (c) EDA-functionalized PES/SAPO-34 mixed matrix membrane.

### CONCLUSIONS

SAPO-34 zeolite has been successfully functionalized using EDA. The presence of amino groups in the zeolite structure has been confirmed by FTIR. The presence of EDA-functionalized SAPO-34 in the MMM

has increased the thermal stability of the membrane as shown in TGA analysis. The images of the membrane's cross-section obtained through FESEM analysis has revealed that the interphase between SAPO-34 particles and PES polymer becomes better if EDA functionalized



zeolite is used. This suggests that EDA also shows a promising property that can improve the zeolite/polymer compatibility. Hence, it is expected that modification of PES/SAPO-34 MMM using EDA would increase the CO<sub>2</sub>/CH<sub>4</sub> gas separation performance compared to the unmodified MMM.

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