AJCHE 2012, Vol. 12, No. 1, 51 – 58

A Comparison of Carbon Molecular Sieve (CMS) Membranes with Polymer Blend CMS Membranes for Gas Permeation Applications

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In this work, polyetherimide (PEI) was used as a main precursor to prepare carbon molecular sieve (CMS) membranes coated on a porous α-alumina disk via inert pyrolysis process. The PEI precursor was modified by blending with poly(ethylene glycol) (PEG) and its effect on the gas transport property of carbon membrane pyrolyzed at 873K was examined. The coating solution was prepared by PEI diluted in N-methylpyrrolidone (NMP) and coated onto support by dip-coating technique. Uniform CMS membranes were obtained by repeated dip-coating and pyrolysis of PEI and PEI/PEG. The structure and the single gas permeation properties of PEI and PEI/PEG CMS membrane were investigated.The thermal stability of CMS membranes prepared was determined by thermal gravimetric analysis (TGA). Elemental analysis, scanning electron microscopy (SEM), and Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy were employed to characterize the resulting membranes. The gas permeation of the CMS membranes was tested using three gases: methane, carbon dioxide, and oxygen and performed at 298K. The best performance was obtained by using PEI/PEG CMS membrane, whereby CO_2 permeability should be $400.44\text{x}10^{-10}\text{mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$.

Keyword: Carbon Molecular Sieve Membrane, Polyetherimide, Polymer Blends, Pyrolysis, Gas Permeation,Separation.

INTRODUCTION

Gas separation membranes have been commercially used in a number of industrial processes such as oxygen and nitrogen enrichment, hydrogen recovery, acid gas treatment and natural gas dehydration (Rao et al. 2008). This gas separation technology offers several advantages over other established techniques such as high productivity, low energy consumption and easy operation (Okui and Saito 1995). Over the last decades, polymeric membranes have been proven to operate in many industrial gas separation processes. However, the current polymeric membranes have reached their limit due to low permeability, flux, chemical stability and temperature limitations (Han et al. 2008). Currently, there is a growing interest in the development of porous inorganic membranes such as silica membranes, zeolite membranes, nanoporous carbon membranes, and CMS membranes. Among these membranes, CMS membranes become promising materials due to their excellent permeation and separation, and thermal and chemical stability under harsh conditions (Kim et al. 2004).

The preparation of CMS membranes involve the following steps; precursor selection, polymeric membrane preparation, pre-treatment, pyrolysis/carbonization, post-treatment and module construction (Saufi and Ismail 2004). Among these steps, the choice of the polymeric precursor is the crucial factor since pyrolysis of different precursor may result in different type of carbon membrane. Besides, pyrolysis conditions (pyrolysis temperature, pyrolysis holding time, heating rate and pyrolysis atmosphere) and post-treatment also affect the gas permeation properties. By controlling pyrolysis conditions of precursor, it is able to produce a series of CMS membranes that posses micropores of desired dimension for a specific separation task. At present, there are numerous polymer precursors being pyrolyzed into CMS membranes; among the most widely used are polyimide and derivatives, polyacrylonitrile (PAN), phenolic resin, polyfurfuryl alcohol (PFA), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), phenol formaldehyde novolac resin (PFNR), polyvinylidene chloride (PVDC), and cellulose.

Today, there are several attempts made to control the pore size and structure of CMS membranes such as modifying the pyrolysis protocol or introducing thermally labile polymers during heat treatment(Han et al. 2008). Pyrolysis of polymer blend which is physical and chemical mixture of more than two different types of polymers having different thermal properties will lead to the formation of porous structure since the thermally labile polymer completely decomposed at a lower temperature compared to decomposition temperature of thermally stable polymer (Lee et al. 2007). In addition, polymer blends technique can improve gas separation performance that not found in a single polymer. This can also promote mechanical strength, chemical resistance and thermal stability, thus stabilizing the gas transport properties (Xing and Ho 2009). There are few thermally labile polymers are considered as pore-forming agents such as poly(vinyl butyral) (PVB), PEG, and polyvinylpyrrolidone (PVP). An early work regarding the use of polymer blend as a carbon material precursor was disclosed by Ozakiand co-workers (Ozaki et al. 1997). In recent years, several CMS membranes fabricated from polymer blends have been reported such as by blending PPO/PVP (Lee et al. 2007), PEI/PVP (Rao et al. 2008), PI/PVP (Kim et al. 2004) and PFNR/PEG(Zhang et al. 2007).

The most popular precursor of the reported CMS membranes is related to polyimide and derivatives due to its high thermal stability and excellent gas separation performance (Wang et al. 2003). However, polyimides are very expensive commercial materials and available only on the laboratory scale. One polyimide-based material which can use economically is a PEI. This material has been used to prepare CMS membranes due to its superior strength and chemical resistance (Fuertes and Centeno 1998) as well as impressive separation factors (Salleh et al. 2011). PEG was chose as a pore-forming agent in order to create mesoporous structure.

Thus, in this work, we report on the synthesis and characterization of PEI/PEG CMS membrane. Further the PEI/PEG CMS membrane's performance for CO_2(0.33nm), O_2 (0.364nm), andCH_4 (0.38nm) gas molecules is compared with PEI CMS membrane in terms of permeability and selectivity. All the membranes were characterized by ATR-IR, SEM, EA, and TGA to evaluate the surface morphology and analysis of CMS membranes.

EXPERIMENTAL

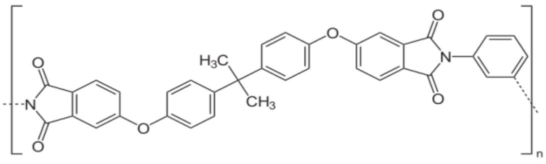
Materials

PEI and PEG ($M_{w.}$ = 1500 g mol^{-1}) were purchased from Sigma Aldrich (M) Sdn. Bhd. The chemical structure of PEI and PEG are shown in figure 1. NMP was purchased from Acros Organics Ltd. The powdered α-alumina was supplied by Inabata & Co. Ltd. Purified O_2 (99.95% purity), CO_2 (99.99% purity) and CH_4(99.99% purity) gases were supplied from Wellgas Sdn. Bhd.

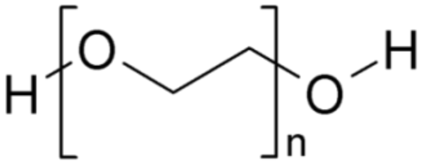
CMS Membrane Preparation

Preparation Of The Porous A-Alumina Disk-Support

The α-alumina powders were thoroughly mixed with defined quantity of distilled water. This mixture was pressed at 1200bar in a static press resulting in disk-shaped of 20mm in diameter and 2.0mm in thickness. The supports were calcined at 1273K for 30h with a heating rate of 1K/min.



(a)



(b)

Fig. 1: Chemical structure of (a) PEI and (b) PEG

Membrane Preparation

PEI CMS membranes were prepared by dissolving 10wt% of PEI in NMP while for PEI/PEG CMS membranes, 5wt% of PEG was added. The mixtures were vigorously stirred for 24h to form homogeneous polymer solution followed by an hour degassing at room temperature. The supports were coated by PEI and PEI/PEG solution by dip-coating technique and pyrolyzed under nitrogen atmosphere. Pyrolysis temperature program consisting of two steps; first step, the precursor was heated from room temperature to 423K and held for 1h with the heating rate 1K/min followed by pyrolysis to a final temperature 873K and holding time of 4h. Then, the membranes were cooled naturally to room temperature.

Gas Permeation Measurement

The gas permeation experiments were done using single gas permeation technique by the variable volume-constant pressure method. This study was done in order to investigate the influence of membrane blending on the gas permeation properties of CMS membranes. CMS membranes were placed inside a stainless steel permeation cell and the samples were covered by plasticine as a sealant to prevent gas leaking during permeation. The gas (O_2, CO_2, and CH_4) was introduced into the upper side of the permeation cell. The feed pressure was set 100kPa and the operating temperature was at 298K. Calibrated soap film flow meter was used to measure the gas permeance penetrate through the membrane. The single gas permeance,P which is defined as the flux normalized by pressure and the membrane area, can be calculated as:

$$P = flux / [(area) \times (pressure)] \qquad (1)$$

The perm selectivity or ideal separation factor of two gas pairs was calculated from the ratio of single gas permeance for the CMS membranes.

Characterization Of CMS Membranes

The functional groups and changes in the chemical structure of PEI and PEI/PEG CMS membranes were studied using ATR-IR spectrometer (IR Prestige-21, Shimadzu) over the wavenumber range of 4000-650cm^{-1}. Elemental analysis of PEI and PEI/PEG CMS membranes were characterized by Elemental Analyzer (Perkin Elmer Series II CHNS/O Analyzer 2400). The weight loss during heat treatment was determined using TGA (Perkin-Elmer TGA 7) at the heating rate of 10K/min from ambient temperature to 1073K under the nitrogen atmosphere. The morphology and surface structure of the membranes were studied by usingSEM(Quanta FEG 450).

RESULTS AND DISCUSSIONS

ATR-IR spectra analysis

Figure 2 shows the typical ATR-IR spectra of PEI, PEI/PEG polymer membranes and their CMS membranes pyrolyzed at 873K. As observed, ATR-IR spectra of PEI polymer membranes obtained do not exhibit significant differences compared with PEI/PEG polymer membranes. Conspicuous peak can be observed at 1716cm^{-1} indicating characteristics of C=O stretching of PEI and PEI/PEG precursor (figure 2(a-b)). Peaks observed at 1600cm^{-1}, 1354cm^{-1}, 1234cm^{-1} were due to aromatic C=C compound, C-N stretching and C-O-C stretches, respectively. These peaks were elongated in figure 2(b) due to the blending of PEI with PEG. After pyrolysis at 873K, all these peaks were disappeared in both CMS membranes (figure 2(c-d)). This result confirms that the polymer structures transformed to amorphous carbon structures during pyrolysis step.

Elemental Analysis

Table 1 shows the results obtained from the elemental analysis of PEI and PEI/PEG CMS membranes and both precursors. It can be observed that when pyrolyzed polymer precursor into CMS membrane, the carbon content increased while oxygen, nitrogen and hydrogen contents were decreased. The polymers degrade during the carbonization and the majority of the heteroatoms were eliminated in this step, resulting in a significant increase in the carbon content of the PEI and PEI/PEG CMS membranes (Laszlo et al. 2000).

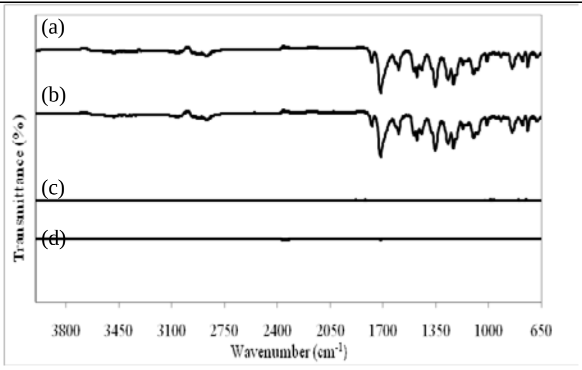


Fig. 2: ATR-IR spectra of (a) PEI precursor, (b) PEI/PEG precursor, (c) PEI CMS membrane, (d) PEI/PEG CMS membrane.

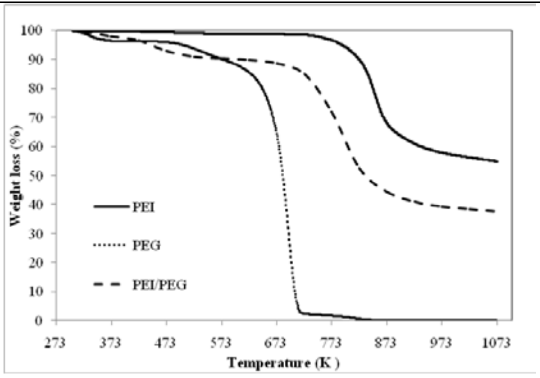


Fig. 3: TGA curves of PEI, PEG and PEI/PEG precursors.

Table 1. Elemental analysis of the polymer precursors and CMS membranes.

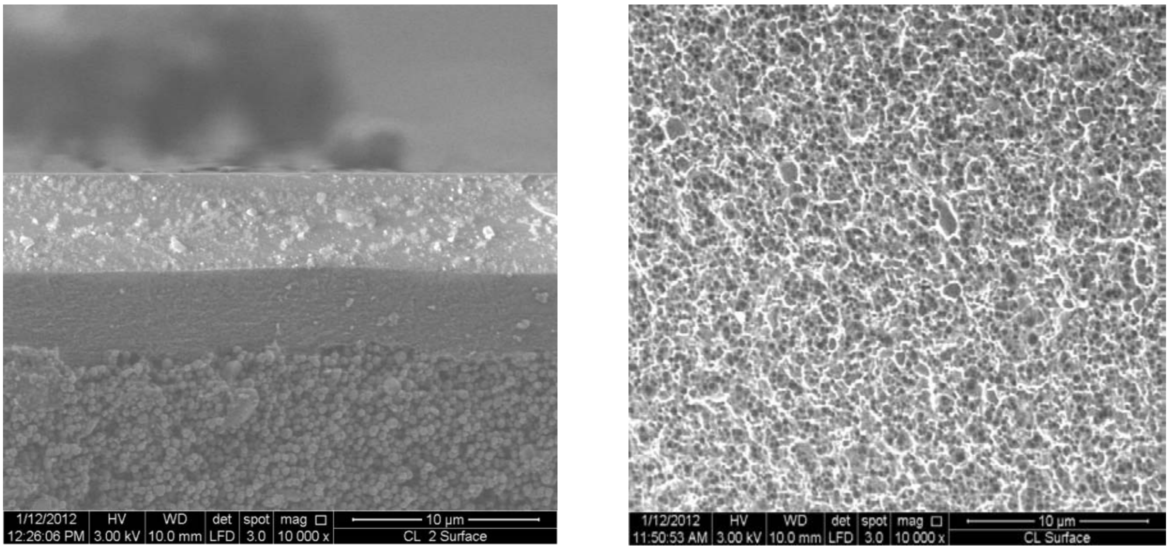
Sample	Element(wt%)			
	Carbon	Oxygen	Nitrogen	Hydrogen
PEI precursor	76.76	14.59	4.54	4.11
PEI CMS membrane	89.43	4.03	4.32	2.22
PEI/PEG precursor	67.27	9.98	17.99	4.76
PEI/PEG CMS membrane	83.81	3.20	10.98	2.01

Thermogravimetric Analysis

Figure 3 shows the weight loss curves of PEI, PEG and PEI/PEG precursors. From the curves, it can be observed that PEI was stable up to approximately 743K before went through the degradation process at temperature between 743K and 873K. For PEG profile, it can be seen that the decomposition process began at 613K and remain almost zero of its initial weight after heating process. The weight residue of PEI/PEG slightly lower compared to PEI which were 37.70% and 54.87%, respectively. This fact indicates that polymer blending lead to a lower thermal stability compared to the pure polymer (Filip and Macocinschi 2002). The curve of PEI/PEG exhibits three stages of weight loss at temperatures of 373, 493 and 723K. The first weight loss was associated to removal of adsorbed water and residual NMP solvent. The second and third weight losses were attributed to the PEG degradation and the decomposition of the PEI main chains, respectively. Besides, it can be seen that PEI/PEG decomposed at lower temperature compared to pure PEI. This might due to the occurrence of interactions between the blends component which leads to less stable structures than the pure polymer. Furthermore, different thermal degradation behaviors of PEI, PEG and PEI/PEG will offer the possibility to the creation of different porous CMS membranes through removal of PEG during the pyrolysis (Zhang et al. 2007).

Scanning Electron Microscopy

The SEM images of cross section and top view of PEI/PEG CMS membrane pyrolyzed at 873K are shown in figure 4. From the cross section (figure 4(a)), three distinct layers which are carbon layer, intermediate



(a) (b)

Fig. 4: SEM micrographs of PEI/PEG CMS membrane: (a) cross section view; (b) top view.

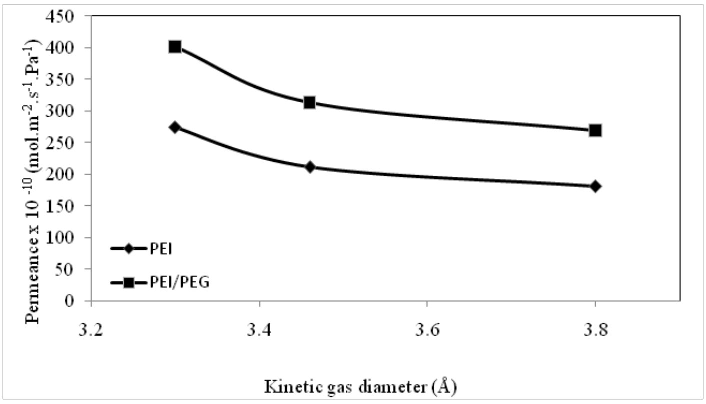


Fig. 5: Gas permeance versus kinetic diameter of gas molecules.

layer and porous alumina support can be distinguished. The carbon film is a dense layer, having a symmetric structure with a thickness around 5μm. For the top layer (figure 4(b)), many pores can be found. According to TGA analysis, decomposition of PEI/PEG began at 723K.Pyrolysis of PEI/PEG at 873K contributes to the pore development whereas at temperature 973-1073K, the pores went through the enlargement process. Heating to the higher temperature (≈1273K) will cause the pores to shrink and disappear (Centeno et al. 2004).

Gas Permeation Properties Of The PEI And PEI/PEG CMS Membrane

Figure 5 shows the permeance as a function of gas kinetic diameter. From the graph, it can be seen that the gas permeation rate of the CMS membranes was higher when blending with PEG. It is assumed that the blending of PEI and PEG provides an enhanced transport of gas molecules. The permeation rate of gas through the membranes was correlated with the kinetic diameter of respective gases.From thefigure, the gas permeance of the chosen gases were in the order of CO_2>O_2>$CH_4$for both CMS membranes. This

Table 2. Gas permeability and selectivities measured at 298K for PEI and PEI/PEG CMS membranes.

Sample	Permeability (x 10 $^{-10}$ mol.m^{-2}.s^{-1}.Pa^{-1})			Selectivity	
	CO_2	O_2	CH_4	CO_2/CH_4	CO_2/O_2
PEI	274.08	210.83	180.31	1.52	1.30
PEI/PEG	400.44	312.84	268.75	1.49	1.28

indicates the presence of a molecular sieving effect in CMS membranes.The result obtained has agreed with those reported by Zhang and co-workers (Zhang et al. 2007). Table 2 shows the selectivity of PEI and PEI/PEG CMS membranes. The permeance of CO_2 was 274.08x10^{-10}mol.m^{-2}.s^{-1}.Pa^{-1} for PEI CMS membrane and increased significantly to 400.44x10^{-10}mol.m^{-2}.s^{-1}.Pa^{-1} for PEI/PEG CMS membrane. The PEI CMS membrane exhibits CO_2/CH_4 selectivity of 1.52, and CO_2/O_2 selectivity of 1.30. For PEI/PEG CMS membrane, CO_2/CH_4 and CO_2/O_2 selectivities drop to 1.40 and 1.28, respectively. The increasing of permeability and decreasing of selectivity were due to the decomposition of thermally labile polymer (PEG) which leads to CMS membrane with larger micropores.

CONCLUSION

The PEI/PEG CMS membrane prepared have higherpermeability of CO_2, O_2, and CH_4compare to PEI CMS membrane. The CO_2 permeation rate was increased significantly from 274.08x10^{-10} mol.m^{-2}.s^{-1}.Pa^{-1} for PEI CMS membrane to 400.44x10^{-10}mol.m^{-2}.s^{-1}.Pa^{-1} for PEI/PEG CMS membrane. This suggested that PEG offered a favorable effect on increasing gas permeability by decreasing the gas diffusion resistance.

ACKNOWLEDGEMENTS

The authors wish to thank the financial supports from USM Membrane Cluster Grant and Ministry of Higher Education (MyPhD).

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