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Enhanced Co_2 Removal Using Polyethersulfone Incorporated with Beta-cyclodextrin/Carbon Nanotubes

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This study was conducted to prepare a mixed matrix membrane (MMM) and to test the performance of the prepared MMM for CO_2 and CH_4 gas separation. MMM containing polyethersulfone (PES) and multi-walled carbon nanotubes (MWCNTs) was prepared by a dry-wet phase inversion technique using a pneumatically-controlled membrane casting machine. The surface modification was performed on MWCNTs in order to enhance the selectivity of CO_2/CH_4. The surface modification of MWCNTs using chemical and physical approaches has been adopted. Mixed acid (HNO_3/H_2SO_4) and β-CD were used for chemical and physical approaches, respectively. Effects of surface modification on MWCNTs/PES MMM were investigated. MWCNTs/PES MMMs were characterised using scanning electron microscopy (SEM), the Fourier Transform Infrared (FT-IR) spectroscopy and pure gas permeation test. The permeability and selectivity, which are the parameters describing membrane performance were calculated via the data obtained from pure gas permeation test with the feed pressure difference from 3 to 7 bars. In this study, surface modified MWCNTs/PES MMM using mixed acid and β-CD has successfully enhanced the CO_2/CH_4 selectivity by 40.6% compared to that of neat PES.

Key words: Multi-walled carbon nanotubes; polyethersulfone; mixed matrix membrane; surface modification; gas separation

As energy cost and demand rise, membrane technology for separating gas is playing an important role in reducing the cost and environmental impact of industrial process. Conventional technologies such as the cryogenic distillation of air, removal of condensable organic vapours from gas mixtures through condensation, and removal of condensable organic vapours from mixtures as well as acidic gases using amine absorption require a gas-to-liquid phase change in the gas mixture that is to be separated.

The phase change adds a significant energy cost to the separation cost. Membrane gas separation, on the other hand, does not require a phase change (Freeman 1999). Nevertheless, polymeric membrane for gas separation has shown severe disadvantages that limit its application. The performance of polymeric membrane is badly reduced when they are used in harsh environment for long period of time.

However, for a membrane to be applicable in separation process industries, it is essential to have highly permeable and selective, flexibility and durable membranes in order to reduce the operation cost in industry. Mixed matrix membrane, comprising rigid permeable or impermeable particles such as zeolites, carbon molecular sieves, silica and carbon nanotubes dispersed in a continuous polymeric matrix presents an interesting approach for improving the separation properties of polymeric membranes (Aroon *et al*. 2010).

Since MMM is a potential membrane for gas separation process, researches have been conducted to mitigate the fabrication and characteristic of different types of

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MMMs to achieve optimum permeability and selectivity. Successful development of these materials would provide a solution to the notorious permeability/selectivity tradeoff observed in polymeric membranes. Arguably the most challenging hurdle that hindering the further development of MMMs is the material incompatibility such as inadequate adhesion. To date, three main approaches were made to improve the permeability/selectivity tradeoff by improving polymer/sieve adhesion: (i) synthesis of new polymers or functionalisation of some present polymers, (ii) development of membranes with more selective materials, and (iii) preparation of composite membranes, where inorganic fillers with specific characteristics are dispersed into polymeric materials (Clarizia *et al*. 2004).

Over the past 25 years, few attempts to increase gas separation membrane performance with a MMM consist of zeolite and rubbery or glassy polymers have been reported. In facts, early research has been done by adding 5A zeolite in silicone rubber which showed it did substantially increase the time lag by immobilising adsorption of CO_2 and CH_4 but only slightly affected the steady-state permeation (Paul & Kemp 1973). Ismail *et al*. (2011) have investigated the effects of purification, functionalisation and multi-walled carbon nanotubes loading in the PES matrix from 0.5-3.0 wt.% and found that MMM embedded with purified and functionalised multi-walled carbon nanotubes possessed better performances in terms of permeability and selectivity in comparison to raw MWCNTs. The highest gas selectivity was achieved at 0.5 wt.% MWCNTs loadings ($\alpha_{CO2/CH4}$ = 250.13; $\alpha_{O2/N2}$ = 10.65). The recent study of Singh et al. (2011) showed that graphene could be used as a viable and inexpensive filler substitute for CNTs in nanocomposite owing to the excellent in-plane mechanical, structural, thermal and electrical properties of graphite

According to Coleman *et al*. (2003), CNTs have the ability to overcome the mechanical weakness of a polymer material even at very low concentration of polymer matrices. This excellent performance is arise due to the presence of carbon-carbon bond in the graphite layer, which are most probably the strongest chemical bond known in nature. Utilisation of CNTs as fillers in a polymer matrix undoubtedly gives a vivid impression on its potential towards hybrid membranes. Therefore, the main purpose of this study is to prepare a mixed matrix membrane using PES as polymer matrix and MWCNTs as the filler. However, there are some concerns on interfacial interaction between the nanotubes and polymer matrix. It was mainly due to the characteristics of MWCNTs such as small diameter, high aspect ratio and large surface area that have indirectly weakening the effect of MWCNTs as filler in polymer matrix. In response to that, the MWCNTs were purified with mixed acid (H_2SO_4/HNO_3) and functionalised with beta-cyclodextrin (β-CD) to facilitate their dispersion in the PES matrix.

EXPERIMENTAL

Materials

PES was purchased from Solvay Advance Material (USA) and used as polymer matrix for PES-MWCNTs MMM. MWCNTs WERE manufactured by catalytic chemical vapor deposition (CCVD) process using an in-house built system with the purity of 65% were used as inorganic filler. β-CD with purity of 97% is obtained from Sigma. Other chemical reagent such as N-methyl-2-pyroliddone (NMP), ethanol (EtOH), sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were purchased from Merck.

Purification of MWCNTs

Prior to the preparation of MMM, MWCNTs were first treated with acid mixtures to remove carbonaceous impurities such as catalyst particles (amorphous carbon), nanocrystalline graphite and metallic catalyst. For this purpose, proper amounts of MWCNTs were dispersed to the acid mixture inside a round bottom flask with 3:1 ratio of H_2SO_4 and HNO_3 respectively.

Functionalisation of MWCNTs

The functionalised MWCNTs (fMWCNT) were prepared by dispersing it in β-CD. The mixtures were ground with a known amount of ethanol until a homogeneous powder is achieved. They were then further mixed through a ball milling process. This procedure resulted in a fine homogeneous cyclodextrin functionalised MWNTs powder.

Dope Preparations

The polymer dope solution is prepared at a 200 g basis and consist of 30 wt.% PES and 70 wt.% NMP were prepared. 0.2 wt.% MWCNTs was prepared based on total solid content. The fabrication procedure for the MMM was identical to the pure polymer membrane preparation with the additional step of incorporating MWCNTs.

Mixed Matrix Membrane Film Formation

The PES/fMWCNTs MMMs were prepared according to the dry-wet phase inversion technique using pneumatically-controlled membrane casting machine which further discussed below. Details on the procedure are explained elsewhere (Kim *et al*. 2007).

Gas Permeation Test

The MMM films were tested on pure CO_2 and CH_4 gas. In this research, the feed pressure was set in the range of 3-7 bars and 298K, and performed at 100% stage cut where the back pressure valve at the retentate side was fully closed. The gas flow rates at the permeate stream were measured by means of soap bubble flow meter reading. Prior to measurements, the system was allowed to attain steady state condition for 30 min (Jomekian *et al*. 2011). This permeation test was repeated for three times and the average was determined. The transport of gases through the membrane can be expressed as permeability, P_A.

$$P_A = \frac{N_A \cdot l}{\Delta p_A}$$

Since the thickness of the selective skin for asymmetric films and fibers often cannot be determined a quantity called the permeance is normally used to indicate the flux. Permeance is equal to permeability divided by the thickness of the selective separation layer. Gas separation unit (GPU) is used to express the permeance.

$$\text{Permeance, } \frac{P_A}{l} = \frac{N_A}{\Delta f_A}$$

$$1 \text{ GPU} = 1 \times 10^{-6} \frac{cm^3(STP) \cdot cm}{s \cdot cm^2 \cdot cmHg}$$

The efficiency of the membrane to enrich one gas over another in the permeate stream can be evaluated by using a quantity known as separation factor which is also known as ideal selectivity or permselectivity and it can be expressed as the ratio of the permeabilities of the penetrate gases A and B:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

Characterisations

The electron micrographs were obtained by using scanning electron microscopy (SEM). SEM is a commonly used characterisation tool to monitor the structure morphology of a MMMs. SEM is also used to observe the compatibility between the sieves and the polymer matrix. In this study, SEM was used to determine the morphology of PES-MWCNTs MMMs. Fourier transform infrared spectroscopy (FTIR) is a tool that used to detect the existence or changes of the functional group in a membrane film. This characterisation method was used to determine the compatibility of the compatibility of PES, MWCNTs, mixed acid and β-CD. Peaks shifting and intensity changes determine the degree of compatibility achieved.

RESULTS AND DISCUSSIONS

Effect of Purification and Functionalisation of MWCNTs on the MMM Morphology

In order to further investigate the effect of purification and functionalisation of MWCNTs on the dispersion of MWCNTs in polymer matrix, SEM characterisation was carried out. SEM was used to characterise the surface morphology of the membrane. Membrane morphology is the main factor that affects the separation properties of a pressure-driven membrane. The SEM micrographs of the surface and cross section morphology for neat PES, as-grown MWCNTs/PES, purified MWCNTs/PES and β-CD functionalised MWCNTS/PES MMMs are shown in Figure 1 and Figure 2, respectively.

From the surface morphology examination, significant defect was observed on the surface layer of neat PES and as-grown MWCNTs/PES MMMs as a thick dense skin and large pore holes are noticeable on the non-uniform structure. The appearance of unselective voids which indicated that the nanotubes were not completely adhere at the surface of the polymer matrix. Added to that, owing to the CNTs inert nature, MWCNTs tend to form bundles with each other and thus do not dispersed well in the polymer matrix. As depicted in Figure 2(c), purified MWCNTs/PES MMMs showed homogeneous mixture and better dispersion of MWCNTs in the polymer matrix, hence resulted a higher viscosity MMMs polymer solution and reduce in the number of pore holes. As a result, purified MWCNTs/PES MMMs showed a less defect skin layer as shown in the SEM micrographs of Figure 6a. Acid-modified MWCNTs have better affinity in mixed matrix membrane than the unmodified MWCNTs because acid-modified MWCNTs formed hydrogen bonds with the C=O groups of the PES molecules (So *et al*., 2007).

Both neat PES membrane and as-grown MWCNTs/PES MMMs displayed cross sectional with a long finger like macro-voids from the skin layer to the support region (Figure 2a and 2b). The formation of larger finger-like structure resembles pore holes. The formation of finger-like structures is the result of the difference of the rate of precipitation and also viscosity of the polymer-blend solutions (Porter 1990). The more viscous solution will result in a more uniform structure while a high precipitation rate and rapid solvent exchange process would lead to a non-uniform finger-like structure. The purified and β-CD functionalised MWCNTs/PES MMMs have resulted in the formation of finger-like structures which resulted from the enhanced compatibility between the inorganic and organic phases (Figure 2c and 2d). It is suggested that the addition of β-CD in MWCNTs does not affect the skin layer of polymer. Comparing to purified MWCNTs/PES MMMs, it can be seen that smaller or thinner finger-like structures were formed with addition of β-CD into MWCNTs.

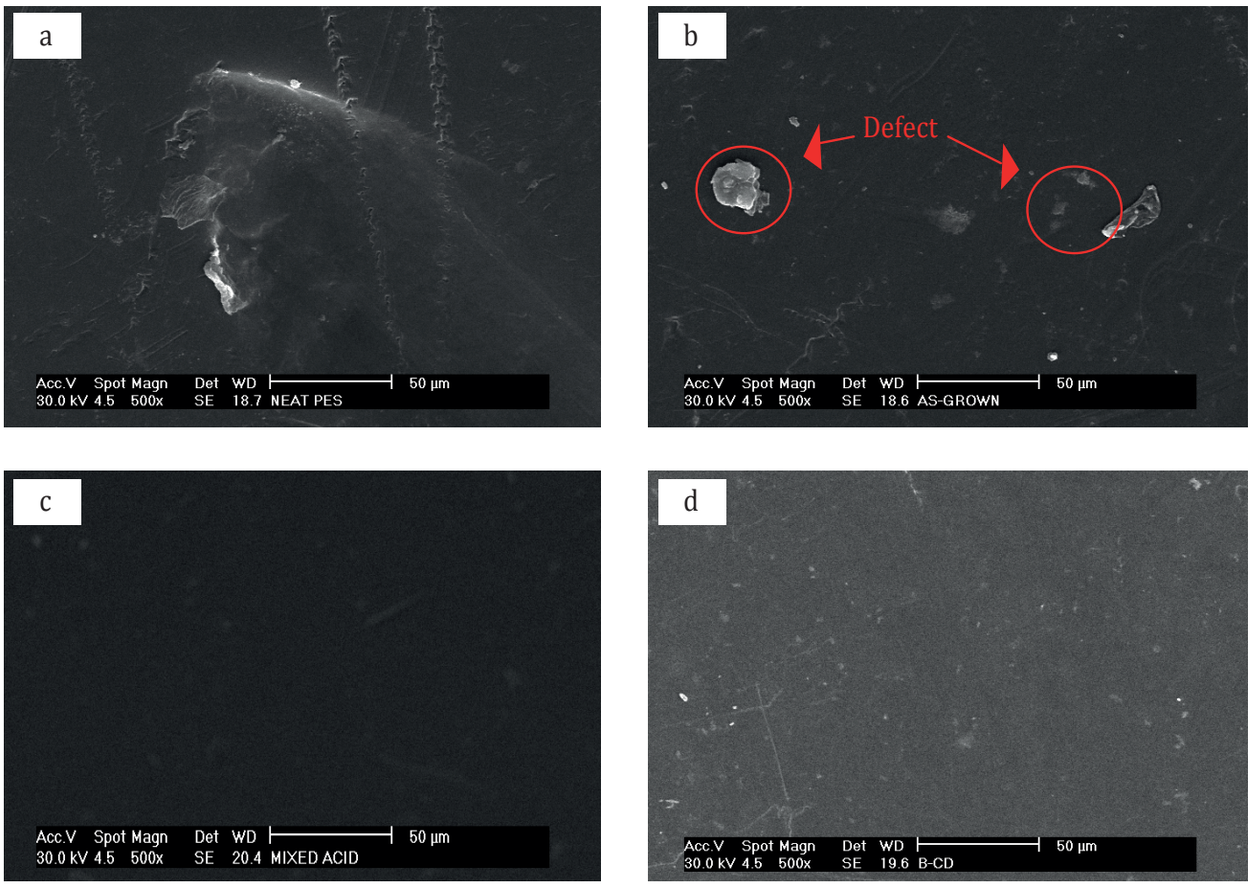

Figure 1. Surface morphology of a) neat PES membrane, b) as-grown MWCNTs/PES MMMs, c) mixed acid-MWCNTs/PES MMMs and d) mixed acid-β-CD-MWCNTs/PES MMMs.

Overall, addition of as-grown MWCNTs into PES polymer matrix has introduced large pore holes and it is not completely adhere at the surface of polymer matrix. By modifying MWCNTs using concentrated mixed acid, pore holes are reduced and better interaction between PES and MWCNTs are formed. Functionalisation using β-CD has further increased the compatibility of MWCNTs in PES polymer matrix and resulted in the formation of more uniform finger-like structures.

IR- analysis

The IR analysis gives a representation of the presence of peaks associated with the modification with both chemical and physical approaches that have taken place with MWCNTs. Figure 3 shows the spectra of MWCNTs and the MMM. Like graphite, the FTIR spectrum of as-grown MWCNTs showed no significant peaks. The peaks appeared at 2923.23 cm^{-1} and 2851.51 cm^{-1} are corresponded to the C-H stretching mode that were attributed to the defects at the sidewalls. The spectrum of mixed acid/ MWCNTs confirmed that the MWCNTs have been modified using strong mixed acid. The peaks at 1627.17 cm^{-1} is corresponded to C=O stretching. The two weak peaks at 2852.53 and 2922.32 cm^{-1} can be assigned to the –CH stretching mode. The broad peak appeared at 3419.59 cm^{-1} can be ascribed to –OH stretching vibration in –COOH group.

Figure 3(c) shows the spectrum of β-CD/MWCNTs. The peaks appeared at 2930–2848 cm^{-1}, 3365.97 cm^{-1} and 1635.09 cm^{-1} are corresponding to the –CH, -OH and C=O stretching mode respectively. The intensity of -CH and C=O functional group peaks decreased due to the increased β-CD/MWCNTs bonding which confirmed the attachment of β-CD with MWCNTs (Sanip *et al*. 2011). Meanwhile, the intensity of the peak appeared at 3365.97 cm^{-1} increased due to the stretching vibration of O–H that shows the characteristics of β-CD. The peaks appearing at 1180 to 1170 cm^{-1} are assigned to β-CD which resulted from C–O–C stretching of α-pyranose group whilst the C–O–H stretching vibration of α-pyranose can be observed in the range of 1100 to 1000 cm^{-1}. The presence of these

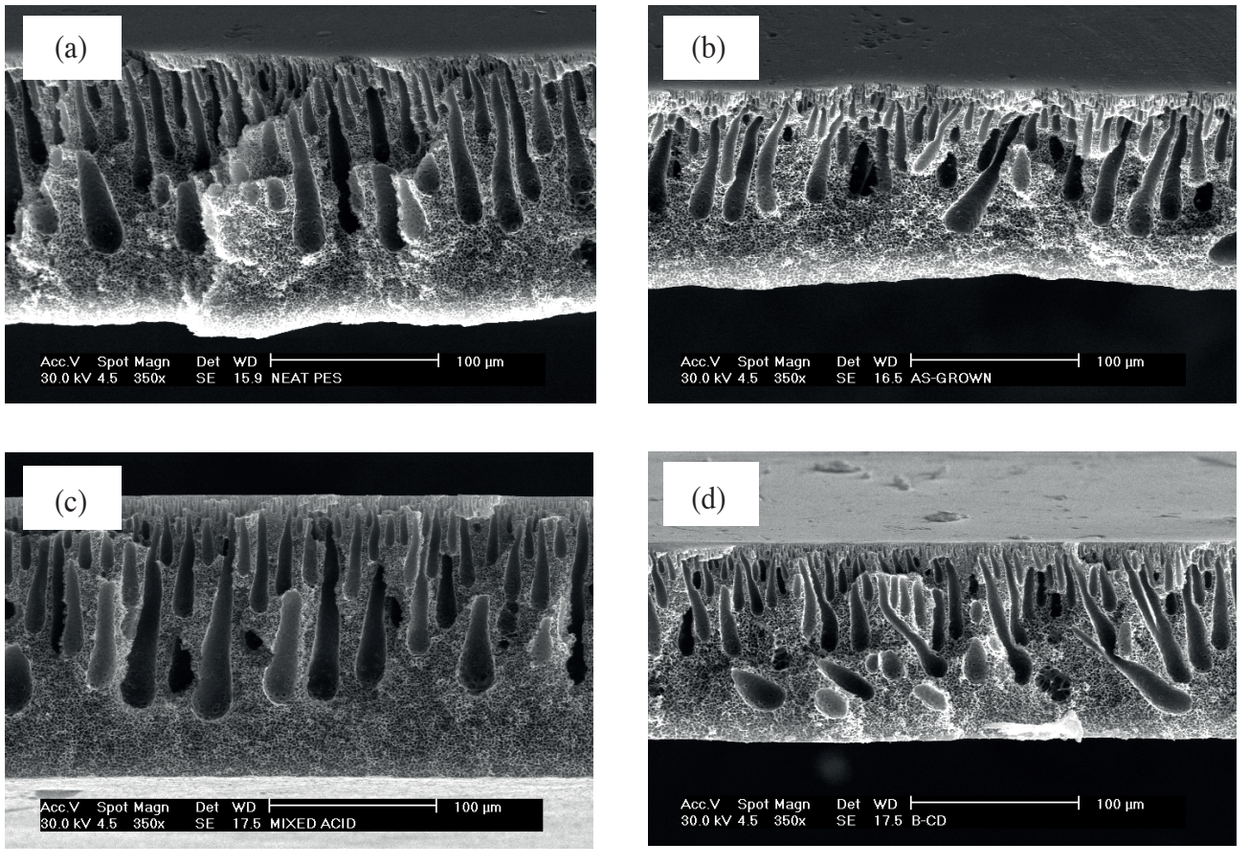

Figure 2. Cross section morphology of a) neat PES membrane, b) as-grown MWCNTs/PES MMMs, c) mixed acid-MWCNTs/PES MMMs and d) mixed acid-β-CD-MWCNTs/PES MMMs.

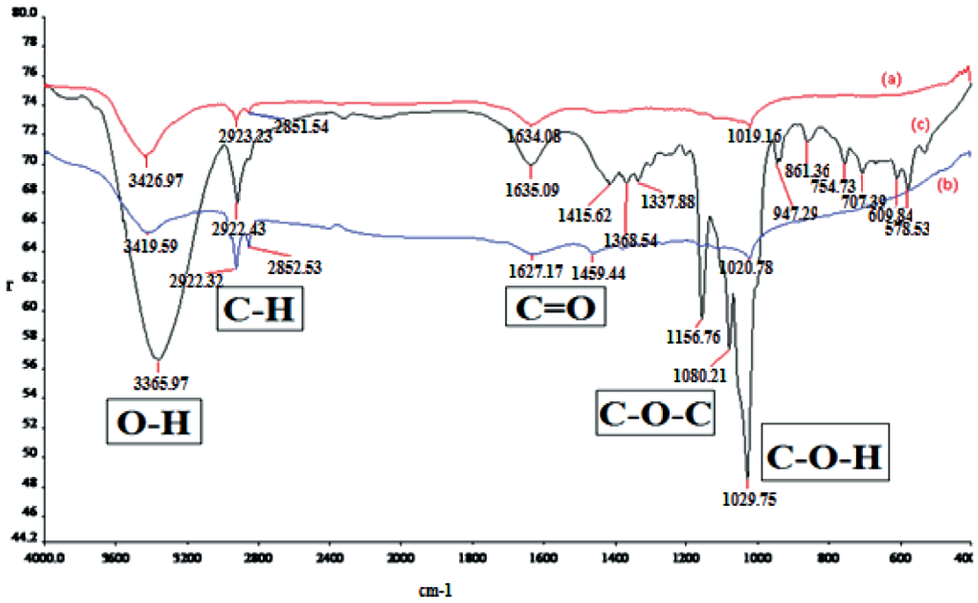

Figure 3. FTIR spectra of (a) as-grown MWCNTs, (b) acid modified MWCNTs and (c) β-CD / MWCNTs.

vibrational peaks confirmed that β-CD has been attached to the surface of MWCNTs. The presence of β-CD along the side walls of the MWCNTs have created organic sites that are able to integrate with the polymer matrix. The attachment of the β-CD onto the surface of the MWCNTs is assumed to be either van der Waals interaction or covalent bonding as a result of the interaction between carbons in the MWCNTs and the hydroxyl functions of β-CD adjacent molecules.

Effects of Purification and Functionalisation of MWCNTs on the MMM Gas Separation Performance

In the gas separation performance, one of the most important criteria to determine the performance of a membrane is the ability of the membrane to exhibit enhancement in gas separation performance. The membrane effectiveness in the gas separation performance was determined by the membrane permeability and selectivity for tested gas CO_2/CH_4 (Kusworo *et al*. 2010). The gas permeation properties of MMM was investigated by embedding 0.2 wt.% of purified and purified/β-CD functionalised MWCNTs in 29.8 wt.% of PES matrix. The gas permeation test was carried out at pressure in the range of 3 – 7 bars. The permeability and selectivity of neat PES and PES/MWCNTs obtained were depicted as Figure 4 and 5, respectively. The use of as-grown MWCNTs, purified MWCNTs and purified/β-CD functionalised MWCNTs as inorganic fillers in MMMs was carried out to investigate the effect of these inorganic fillers to the gas performance.

As shown at Figure 4, the gas permeability increased with the testing pressure. It can be observed that the permeation rate increased in the order of CO_2 > CH_4. The increased permeability showed that mainly Knudsen mechanism controlled flow through the pores. The gaseous concentration in the permeate steam increased with the feed pressure thus led to the increase in membrane permeability. Gases of larger kinetic diameter showed decrease in permeability. Since the kinetic diameter of CH_4 the gas molecules is larger than that of CO_2 (Yong *et al.* 2001), these results indicated that gas diffusivity mechanism mainly depends on the kinetic diameter of penetrants.

The results obtained also showed that MWCNTs incorporated MMMs exhibited higher permeation rate compared to that of neat PES. As discussed earlier, the SEM micrographs of as-grown MWCNTs MMMs indicated the existence of defect sites on the surface of the membrane and also MWCNTs aggregation in the polymer matrix. The high permeability of CH4 for the as-grown MWCNTs – PES MMMs compared to other MMMs was primarily caused by the presence of defect sites on the surface of skin layer and also the formation of narrow gaps surrounding the MWCNTs (Porter 1990). In addition, as-grown MWCNTs were not well distributed in polymer matrix and resulted in the formation of severe unselective voids between the nanotubes and polymer matrix. Hence, the PES polymer chains could not disperse and infiltrate through the spacing between MWCNTs structures.

Therefore, the unselective voids functioned as pinholes that allowed all gases molecules passed through rapidly without any selectivity. Thus, the permeability of all gases increased accompanied with the deterioration of gas selectivity (Mustafa *et al*. 2010). On the other hand, the acid modified MWCNTs MMMs showed the highest CO_2 permeability due to better dispersion of the MWCNTs in polymer matrix. The well dispersed purified MWCNTs in the polymer membrane provides smooth channel to allow gases molecules passed through rapidly. Besides, it also provides a better absorption and transportation of gas molecules. Table 1 shows the gas permeation of neat PES and PES-MWCNTs MMMs.

Functionalisation of MWCNTs using β-CD has enabled higher permeability rate compared to neat PES. MWCNTs functionalised with β-CD provided easy channels or nanoporosity for the permeation of CO2 gas through the membrane. It is due to the attachment of β-CD onto the surface of MWCNTs and resulted interaction between carbons in the MWCNTs and the hydroxyl functions of β-CD adjacent molecules which created better pore entrance/exit effects for CO_2 gas. The addition of open – ended and shortened MWCNTs has also resulted in favourable permeability increase for CO and CH_4. Nevertheless, when compared to acid modified MWCNTs/PES MMMs, lower permeability was observed. It may due to thee better adhesion of MWCNTs with the polymer matrix at the surface that has provided enhanced absorption of CO_2 and CH_4.

Figure 5 demonstrates the effect of MWCNTs on MMMs selectivity. The as-grown MWCNTs MMMs showed lower selectivity than that of neat PES membrane. These results were in agreement with the SEM image that showed the existence of defect sites and narrow gaps surrounding CNTs where gas molecules can pass through without selectively separate the gas molecules (Cong *et al*. 2007).

Meanwhile, the acid modified MWCNTs MMMs showed slight improvement of selectivity over neat PES. One of the plausible reasons is due to the well dispersion of acid modified MWCNTs in PES matrix which has allowed the casting of defect-free surface's membrane. The incorporation of acid modified CNTs in MMMs improved the compatibility of CNTs and polymer. During the acid treatment, strong mixed acid (5M) has removed the impurities of MWCNTs such as metal catalysts. Functional groups such as hydroxyl and carboxyl groups were introduced to the MWCNTs which indirectly improve their compatibility to the PES (Goh *et al*. 2011). Thus, no gases passed through the gaps between CNTs and polymer,

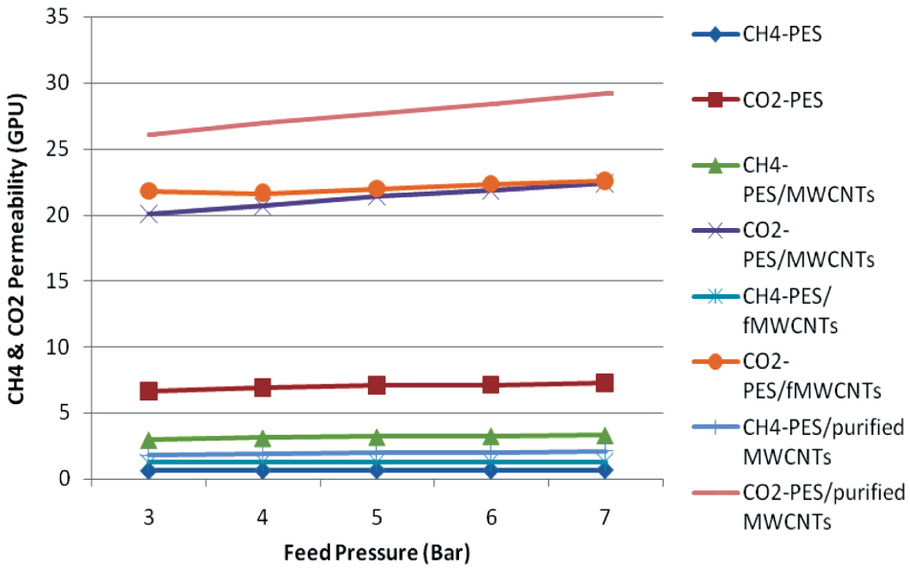

Figure 4. Effect of surface modification on MWCNTs for permeability of CH_4 and CO_2 at different pressure.

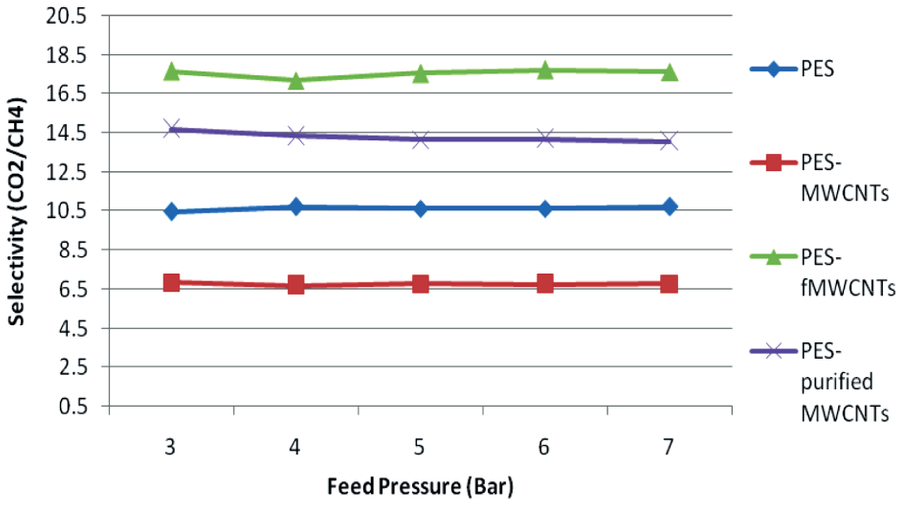

Figure 5. Effect of surface modification on MWCNTs for CO_2/CH_4 selectivity at different pressure.

the separation of gases was increased when gases passed through the CNTs with a certain diameter size (Cao & Wu 2004).

β-CD has been applied to overcome the drawbacks of chemical modification that might potentially damage the MWCNTs structures, which eventually might lead to the deterioration of its intrinsic properties. β-CD is cyclic oligosaccharide of 6-8 glucopyranoside units which can be represented as toroids with an inner cavity if several angstroms in diameters (Jianga & Chung 2009). β-CD molecules consist of 2 rims of hydroxyl groups at primary (tail) and secondary (head) which can either react with substrates themselves or be used to attach to a polymer chain (Jomekian *et al*. 2011). The unique characteristics of β-CD has promoted it a suitable candidate for the functionalisation of MWCNTs. MWCNTs functionalised with β-CD has improved the dispersion in MMMs and changed the chemical affinities of penetrants which will indirectly improved gas separation properties. Figure 5 shows that MWCNTs that functionalised using β-CD exhibited the highest selectivity. The fine porosity of

TABLE 1. CO_2 GAS PERMEANCE (GPU) OF NEAT PES AND PES-MWCNTS MMMS.

Pressure (bar)	Neat PES	As-Grown MWCNTs	Purified MWCNTs	Purified and functionalised MWCNTs
3	6.61±0.1311	20.03±0.0721	26.07±0.1212	21.75±0.1323
4	6.89±0.1249	20.64±0.0701	26.94±0.0872	21.62±0.0654
5	7.09±0.0794	21.42±0.1389	27.74±0.0954	21.94±0.1600
6	7.11±0.1114	21.83±0.0916	28.45±0.1652	22.33±0.1323
7	7.26±0.0361	22.39±0.0954	29.24±0.1389	22.55±0.1908

TABLE 2. SELECTIVITY OF CO_2/CH_4 FOR NEAT PES AND PES-MWCNTS MMMS.

Pressure (Bar)	Neat PES	As-Grown MWCNTs	Purified MWCNTs	Purified and functionalised MWCNTs
3	10.49	6.86	14.69	17.65
4	10.73	6.70	14.34	17.21
5	10.64	6.78	14.16	17.56
6	10.63	6.75	14.20	17.74
7	10.74	6.80	14.08	17.62

β-CD/MWCNTs has allowed CO_2 gas passed through the membrane easily. Figure 7b shows that addition of β-CD has resulted more open ended and shortened MWCNTs that in favorable of CO_2 permeability. Purification and β-CD modification on MWCNTs have improved the selectivity by 40.6% corresponding to the neat PES. Table 2 shows the selectivity of CO_2/CH_4 for neat PES and PES-MWCNTs MMMs.

CONCLUSION

In this research, the addition of surface modified MWCNTs using mixed acid treatment and β-CD has improved the selectivity of CO_2/CH_4 by 40.6% compared to that of neat PES. It has also increased the permeation rate of CH_4 and CO_2. These results were based on the improvement of the solubility and homogeneous dispersion of inorganic filler in the polymer matrix through the surface modification by chemical and physical approach on MWCNTs. The gas separation of MWCNTs/PES MMMs can be improved through the formation of a strong interaction between the functionalised MWCNTs and PES.

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