



Surface Modification of Carbon Nanotubes Using Acid Treatment to Enhance Gas Separation Performance of Hybrid Nanocomposite Mixed Matrix Membrane

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Abstract: Recently, many researchers have explored the idea of hybrid mixed matrix membranes. Membrane separation processes based on hybrid mixed matrix membrane comprising inorganic material such as zeolite and carbon nanotubes (CNTs) embedded in polymer matrix have become one of the emerging technologies and extensively discussed in membrane separation literature. The present study is performed primarily to investigate the effect of chemical modification on carbon nanotubes surface towards gas separation performance of mixed matrix membrane. Polyethersulfone (PES)-carbon nanotubes mixed matrix membrane for modified and unmodified carbon nanotubes were casted using dry/wet phase inversion technique. The modified carbon nanotubes were prepared by treating the carbon nanotubes with acid treatment to allow PES chains to be attached to carbon nanotubes surface. The results of FESEM, DSC and FTIR analysis confirmed that chemical modification on carbon nanotubes surface had taken place. Meanwhile, the nanogaps in the interface of polymer and carbon nanotubes were appeared in the PES mixed matrix membrane with unmodified of carbon nanotubes. The modified carbon nanotubes mixed matrix membrane increases the mechanical properties, the productivity and purity of gas mixture compare to neat PES and unmodified carbon nanotubes mixed matrix membrane. For PES-modified carbon nanotubes mixed matrix membrane the maximum selectivity achieved for CO₂/CH₄ are 32.59.

Key words: Mixed matrix membrane • Carbon nanotubes • Biogas • Gas separation

INTRODUCTION

In petrochemical industries, varieties of processes are being used for the removal of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) from natural gas. Several basic mechanisms are involved to achieve selective separation of gas constituents. These may include physical or chemical absorption, adsorption on a solid surface, membrane separation, cryogenic separation and chemical conversion. However, membrane separation processes have emerged during the last two decades. This is due to the fact that membrane separation processes may offer more capital and energy efficiency when compared to the conventional separation processes [1-3]. In addition, advantage of membrane technology is its simplicity, *i.e.*

no absorbent, which has to be regenerated; it can be easily retrofitted, modularized and scaled-up for several applications [4].

At the present, polymeric membranes dominate the membrane separation field due to the fact that they are well developed and quite competitive in separation performance and economics. Since the separation of gas mixtures depends on the relative solubility and diffusivities of individual components within a particular membrane, no single material will be dictated by the nature of gas mixture to be separated. Glassy polymers such as polysulfone, polyethersulfone (PES) polyimide and ethyl cellulose which are known to have high mechanical stability and desirable inherent transport properties at high temperature are more commonly used [2].

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Despite concentrated efforts to tailor polymer structure to affect separation properties; current polymeric membrane materials have seemingly reached a limit in the trade-off between productivity and selectivity. Pure polymer membranes are oftentimes shows several limitations as low selectivity, high temperature instability and swelling and decomposition in organic solvents. Hybrid membranes composed organic- inorganic has attracted attention as the future membrane material. The concept of hybrid membranes or mixed matrix membrane combines the advantages of high separation capabilities of the molecular sieves and the desirable mechanical properties and economical processing capabilities of polymers [3-5]. Mixed matrix composite membranes have received world-wide attention in the field of material science in the last 2 decades [2-5]. As the consequence, it has been proposed as an alternative approach to obtain the high selectivity benefits of molecular sieve materials (e.g. carbon molecular sieves (CMS), silica and zeolites) and to counter the costly processing of purely homogeneous molecular sieving membranes through incorporating these sieves into a process able polymeric matrix. Currently, significant efforts have been devoted in fabrication of mixed matrix membrane by using carbon nanotubes as great potential filler [5-6]. The properties of polymer nanocomposites containing carbon nanotubes depend on several factors in addition to the polymer: synthetic process used to produce nanotubes; nanotube purification process (if any); amount and type of impurities in the nanotubes; diameter, length and aspect ratio of the nanotubes objects in the composite (isolated, ropes and/or bundles); nanotubes orientation in the polymer matrix. Kim et al. [7] studied the effect of incorporating of CNTs on polyimidesiloxane matrix on gas separation performance. They observed that the addition of small CNTs to the copolymer matrix will be reducing the permeability helium and hindering the diffusion of nitrogen due to the impermeable properties of CNTs. As the applications for polymer-based organic-inorganic composites membranes expand, new challenges arise. One of these challenges is to synthesize both higher performance membranes that are more durable [8]. Therefore, it is important to overcome these challenges that prevents successful introduction of inorganic molecular sieve materials into an organic polymer matrix. Many studies have been attempted to improve the interaction between the polymer and molecular sieve in order to enhance the separation performance [9-11].

Currently, different approaches are reported to improve the dispersion of CNTs in solvent or polymers in order to fabricate the composite mixed matrix membrane. As a result, extensive research have promoted upon modification, pretreatment or functionalization of their surface. The surface modification has to improve solubility of the CNTs and their ability to mix well in most organic substance. Therefore, in the present study, the feasibility fabrication and characterization result of hybrid nanocomposite membrane using carbon nanotubes particles as selective inorganic fillers was investigated. The carbon nanotubes were functionalized using acid treatment technique. The aim is to get a CNTs linked with the coupling agent having a functional group such as a double bond which can be utilized further for copolymerization. Hence, this reaction product can be chemically explored for improving their compatibility with polymer matrix to increase the separation performance.

MATERIALS AND METHODS

Polyethersulfone was supplied by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120°C overnight before dope preparation; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. The multiwalled carbon nanotubes (MWCNTs) were produced using thermal catalytic chemical vapour deposition (CCVD). The particle size of CNTs was about 25.76 nm. In this study, the polymer solution consists of 25 wt % polymer, 75 % NMP and 1 wt% carbon nanotubes in the total solid. Mixed matrix membranes were prepared according to the dry/wet phase inversion technique. The solution was poured on a clear, flat and smooth glass plate that was placed on the trolley. Stainless steel support casting knife was used to spread the solution to a uniform thickness by pneumatic force. Carbon nanotubes samples were additionally modified by acid treatment. First, the CNTs were treated with hydrochloric acid to remove the impurities. The mixtures of CNTs and hydrochloric acid were stirred using magnetic stirrer for 2 h, then diluted in water, filtered, washed with deionised water and then dried overnight in vacuum at 40°C. Finally, the CNTs were again dried and pre-treated in H₂SO₄ and it is stirred at least for four hours at 40°C. After that, the resulting dispersion was diluted in water and filtered. The resulting solid washed till to neutral pH and the sample was dried overnight in vacuum at 40°C before it was ready to be used in preparation of dope solution.

The membrane sheets were coated with highly permeable elastomeric silicone polymer (Sylgard 184 Dow Corning). The membrane coating was done after the uncoated membranes were tested. The intention of coating is to fill any surface pinholes or defects on membrane surface. Membranes were submerged in a 3% w/w solution of silicone in n-hexane for 24 hours and subsequently placed in oven for 3 days at 120°C to allow curing before permeation testing. A Supra 35 VP Field Emission Scanning Electron Microscopy (FESEM) was used to ensure the asymmetric structure. The glass transition temperature of each cast film was determined using differential scanning calorimetry (Mettler Toledo DSC 822e). A small piece of membrane or pure polymer sample was first stored under vacuum at 100°C for 24 hours to remove adsorbed water; then weighed and placed into aluminium DSC pans. The scanning range was 50- 320°C with scanning rate of 10°C min⁻¹ in the first DSC cycle to remove thermal history and then cooled from 320 to 25°C at the rate of 10°C min⁻¹. Finally the second cycle was carried out with the same procedure.

The permeation test involved the use of gas permeation cell in which the membrane was placed on a sintered metal plate and pressurized at the feed side. Gas permeation rates were measured by a constant pressure system using a soap bubble flow meter. Pressure normalized gas permeation flux or permeance for gas *i*, $(P/l)_i$, in (GPU), can be calculated as follows:

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\Delta p} \quad (1)$$

where Q_i is the volumetric flow rate of gas *i*, Δp is pressure difference across membrane (cm Hg), *A* is membrane affective surface area (cm²) and *l* is membrane skin thickness (cm). The ideal separation factor $\alpha_{i/j}$ can be calculated by using equation below:

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (2)$$

RESULTS AND DISCUSSIONS

Morphology of Asymmetric Polyethersulfone-nanotubes Hybrid Nanocomposite Mixed Matrix Membranes: Primarily, in this study the effect of chemical modification on surface of carbon nanotubes using sulfuric acid for fabricated hybrid nanocomposite mixed matrix membranes

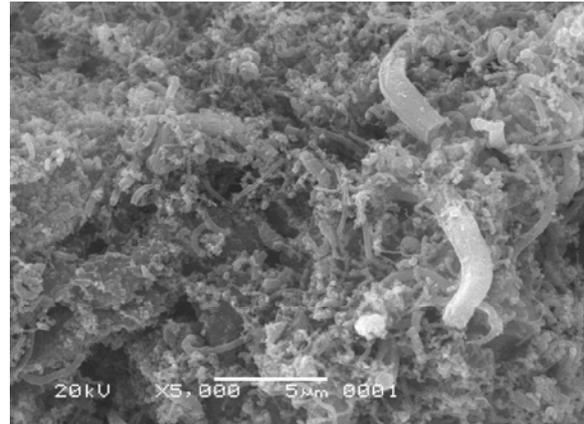


Fig. 1: Cross-sectional FESEM images of unmodified multi walled carbon nanotubes (MWNTs)



Fig. 2: Cross-sectional FESEM images of modified multi walled carbon nanotubes (MWNTs)

were examined. In order to look their characterizations, Field Emission Scanning Electron Microscopy (FESEM) and Differential Scanning Calorimetric (DSC Testing) would be used. Therefore, characterization of the membranes will be discussed after this.

FESEM characterization was used in order to determine the qualitative analysis of hybrid nanocomposite mixed matrix membrane. In order to further investigate the dispersion of the functionalized MWNTs (multi walled carbon nanotubes) in hybrid nanocomposite mixed matrix membrane; careful FESEM inspections were carried out. Normally, natural or unmodified carbon nanotubes are very long tubes and flocks together as shown in the Figure 1. For the FESEM images of treated CNTs with 1 M sulfuric acid, the cross-sectional FESEM images showed a structure of treated CNTs. After CNTs be modified with sulfuric acid, the longer structure becomes shorter and the structure of treated multi walled carbon nanotubes are shown in the Figure 2.

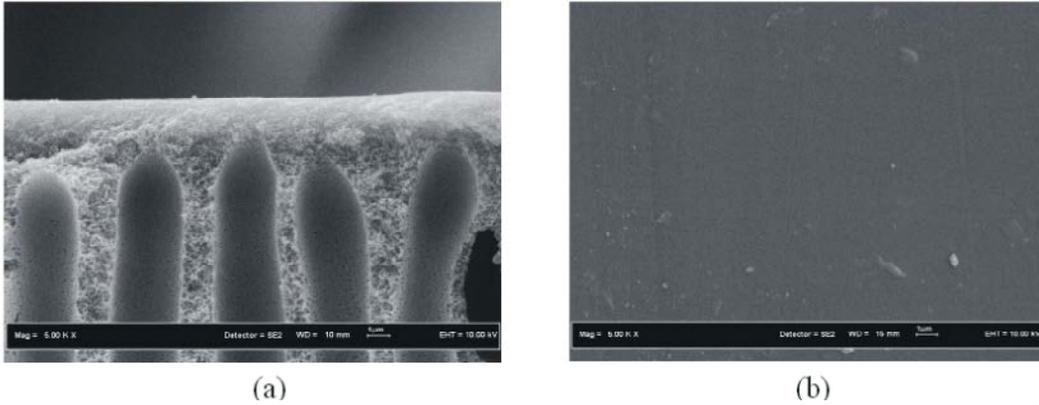


Fig. 3: SEM picture of asymmetric polyethersulfone membrane at the: (a) cross section and (b) outer surface image layer.

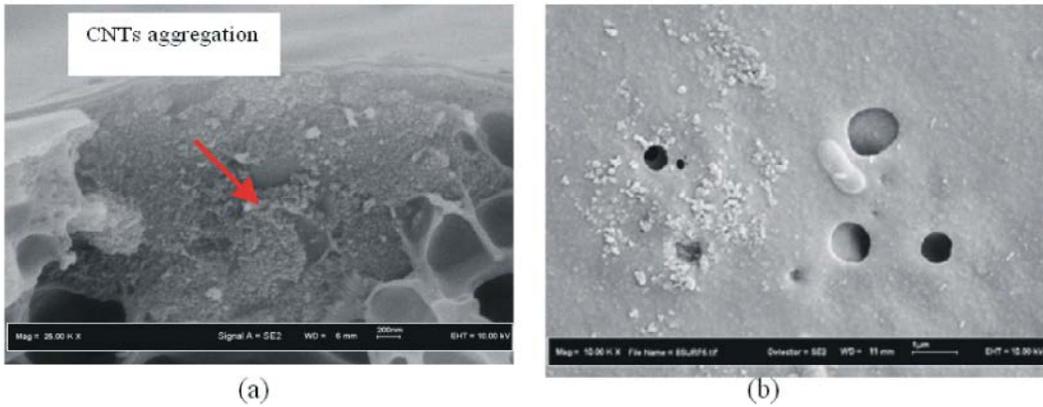


Fig. 4: SEM picture of asymmetric polyethersulfone-unmodified CNTs membrane at the: (a) cross section and (b) outer surface image layer.

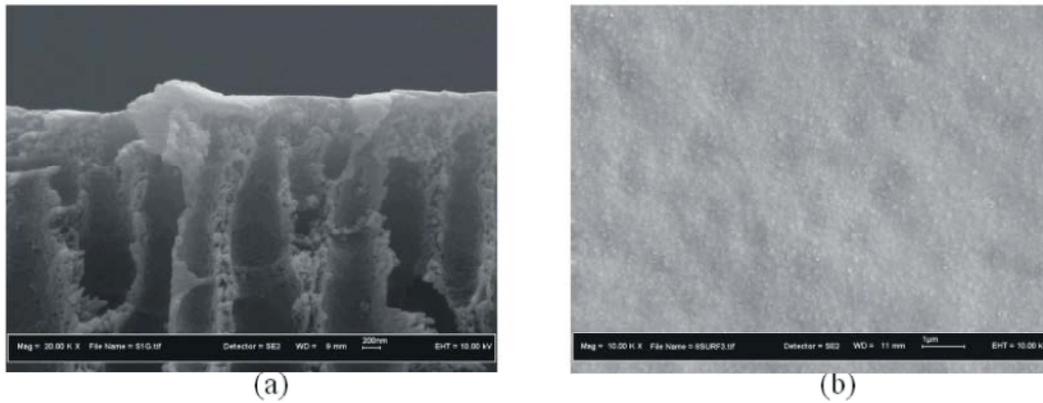


Fig. 5: SEM picture of asymmetric polyethersulfone-modified CNTs membrane at the: (a) cross section and (b) outer surface image layer.

After functionalizing MWNT using sulfuric acid, the MWNTs were expected well distribute on the PES matrix. The functionalized MWNT using sulfuric acid made the carbon nanotubes having short length. Furthermore, it can be dispersed easily into polyethersulfone matrix [12-15]. Usually, carbon nanotubes are closely entangled

and impurities of metal clusters originated from the catalyst stick on the surface of the ropes. These metal impurities on the tips of the ropes can block gas stream when these unpurified samples are used in the hybrid nanocomposite mixed matrix production. Samples in any part seem have to be well purified since most impurities

appear to be removed. However, these purified samples can be highly tangled with one another and are also quite long. In order to use carbon nanotubes in hybrid nanocomposite mixed matrix application, these nearly endless and highly tangled carbon ropes should be cut into short lengths of open tubes. After acid treatment using 1 M sulfuric acid in order to cut ropes, other parts which clearly showed that the length of each rope is now in the shorter lengths so that it could be easily dispersed into the polymer.

As shown in Figures 3-5, there were some differences between unmodified and modified carbon nanotubes. The FESEM micrographs of the cross-sectional and the surface of the neat PES, PES-unmodified nanotubes and PES-modified nanotubes mixed matrix membranes are shown in Figures 3-5. The structure of nanotubes composite membranes showing finger like structure which consisted of a dense skin layer supported by a spongy porous substructure. The unmodified carbon nanotubes particle seemed to good adhere with polymer matrix as shown in Figure 4. The smooth surface of the unmodified nanotubes-PES mixed matrix membrane might be due to the shape of the carbon nanotubes particles appeared to be oblong; therefore, no sharp edges that could easily perforated the active surface skin. However, in the case of unmodified carbon nanotubes, the unselective voids appeared indicated that the carbon nanotubes did not completely adhered on the surface of polymer matrix. The small surface ruptures and aggregation are also occurred on the mixed matrix membrane with unmodified carbon nanotubes as shown in Figures 4a and 4b. As demonstrated in Figures 5a and 5b, the CNTs dispersion into the polymer did not form any agglomeration. This phenomenon might be due to that the modified carbon nanotubes can be suspended and manipulated as individual macromolecules without entanglement in hybrid nanocomposite mixed matrix membrane fabrication. Previous study by Cong et al. [11] stated that the acid-SWNTs were dispersed much better than the unmodified SWNTs in the membranes such as mixed matrix membrane. The uniform nanocomposite membrane was formed and this evidence showed that, increasing loading of acid will disperse carbon nanotubes much better compared to unmodified CNTs and lower loading of acid.

The cross-section and surface of PES-modified CNTs using 1 M of sulfuric acid are shown in Figures 5a and 5b. The porous substrate of the fabricated membrane and the active skin layer can be observed in Figure 5. Cross-section of porous substrate region for PES modified CNT

clearly show the compatibility between modified CNT loading with PES. Moreover, from the cross section can be seen that CNTs clearly act as the filler to in the PES polymer host. Due to the chemical and physical properties of sulfuric acid could be able to enhance the bond strength which provides a stable and strong bond between the modified CNT with PES matrix and finally reduced the presence of voids surrounded on CNT surface. Therefore, the good compatibility between polymer matrix and carbon nanotubes would finally lead to diminish gas penetrants via unselective voids of carbon nanotubes and simultaneously high gas separation performance of membrane is able to be achieved [7, 13-15]. The smooth surface of carbon nanotubes might also induce to enhance the adhesion between the nanotubes and the host of polymer.

Differential Scanning Calorimetry Analysis: The Differential Scanning Calorimetry has been done to indicate whether the CNT-PES blends were indeed miscible by observing the glass transition temperatures of the blend composition. The T_g for each membranes was determined from the heat flow versus temperature curve using an onset method. Table 1 shows the results of PES membrane, unmodified CNTs-PES membrane, PES-CNTs modified with 1 M sulfuric acid.

The influence of acid treatment modification on the glass transition temperature of PES-carbon nanotubes mixed matrix membranes are tabulated in Table 1. In the thermo-gravimetric and differential thermo-gravimetric results of pure and functionalized CNTs should reports on thermal degradation of MWNTs reveal that the on set of degradation starts at around certain temperature, which is attributed to the degradation of grapheme walls with complete degradation at around related temperature [11-12]. As summarized in Table 1, the glass transition value, the acid treatment of functionalized CNT have increased the glass transition temperature T_g . This can be seen in the effect of T_g for CNT modification with acid treatment. Increase in temperature leads to the condensation reaction between the adsorbed sulfuric acid and -OH groups present in the functionalized CNT surface and thereby eliminates water and methanol. The second and third transitions are attributed to the break down of hydrogen bonds and the bonds that present in grafted sulfuric acid leading to a major weight loss.

It can also be seen that compared to neat PES polymer, the T_g of the mixed matrix membranes increased about 3°C with the incorporating only 1 wt% modified carbon nanotubes using 1 M acid treatment into the

Table 1: Effect of acid treatment of CNTs on the glass transition temperature of PES-CNTs mixed matrix membrane

No	Membranes	T _g (°C)
1	PES	218.8
2	Unmodified CNTs	220.15
3	Modified CNTs with 1 M H ₂ SO ₄	221.67

Table 2: Effect of sulfuric acid treatment on the gas separation performance of polyethersulfone-CNTs mixed matrix membranes at room temperature and 5 bars.

Membrane	Single gas permeance (GPU)		Selectivity
	CO ₂	CH ₄	
Neat PES	20.36	0.70	28.75
Untreated membrane	25.18	1.96	12.84
Modified membrane	27.05	0.83	32.59

matrix. This phenomenon indicates that the mobility of polymer chains is reduced due to the restriction effect of carbon nanotubes. This result is in agreement with the previous study [13]. Based on Table 1, it can be concluded that the carbon nanotubes surface modification using acid treatment could induced the adherence between polymer matrix and carbon nanotubes particles. Therefore, it can be concluded that modified carbon nanotubes using chemical modification included into PES matrix makes the composite film stiffer and stronger due to strong interfacial interaction between the nanotubes and PES host matrix. Moreover, addition of the nanotubes the movement of polymer chain in polymer host matrix is restricted and this phenomenon likes physical cross-linking.

Gas Separation Performance of PES-Carbon Nanotubes Mixed Matrix Membrane: In gas separation performance, the criteria which is important in determining whether the membrane are classified as good or not was determined by the ability of the membrane to give the high enhancement in gas separation performance than others membrane. Thus, this testing was carried out in order to study the membrane effectiveness due to the effect of chemical modification on carbon nanotubes surface. The membrane effectiveness in the gas separation performance was determined by the membrane permeability and selectivity for tested CO₂ removal. In this study, we were used gas sample of CO₂ and CH₄. The gas permeation properties for each flat sheet carbon nanotubes mixed matrix membrane were measured by using variable pressure constant volume method. The permeability and selectivity for tested gases CO₂/CH₄ obtained are presented in Table 2.

This table summarizes the permeability and selectivity data of neat PES, PES unmodified and PES-modified CNT.

Generally, the idea to put inorganic filler into organic polymer was enhanced gas permeability of polymer nanocomposites membranes was due to the disturbed polymer chain packing by the nanofillers. Therefore, the well dispersed and good adherence of carbon nanotubes will be effectively increased the gas permeability due to more effectively insert between polymer chains of the matrix. Addition of 1 wt% of modified carbon nanotubes loading to PES resulted in about 32.85 % increases in permeability of CO₂. The main pathways of gas transport through the mixed matrix membranes are through dense layer of PES matrix, highly selective carbon nanotubes and non-selective gaps or voids between the matrix and sieve particles. From FESEM data in Figures 5a and 5b, the carbon nanotubes are well dispersed in polymer matrix and serve as channels to transport gas molecules. The results are consistent with the previous study carried out by Chen and Sholl [16]. Moreover, the permeability for unmodified carbon nanotubes for all gases also increases compared to neat PES membrane. However, the CO₂/CH₄ selectivity was decreased for unmodified carbon nanotubes mixed matrix membrane. Therefore, the increase of permeability in the PES-unmodified carbon nanotubes was not due to the gas transportation inside the nanotubes. As shown in Figure 4, the PES- unmodified carbon nanotubes are not well distributed in polymer matrix and the severe unselective voids between carbon nano-particles and polymer matrix was appeared. Hence, the PES chains could not fall onto the carbon nanotubes walls tightly and forming a narrow gaps surrounding the carbon nanotubes. Therefore, gas molecules can easily passed through the unselective voids or the gaps. The unselective voids would be functioned as pinholes that allow all gases molecules pass rapidly without any selectivity. Thus, the permeability of all gases is increased thus reducing the gas selectivity. As results are summarized in Table 2, the acid treatment could modify carbon nanotubes filled PES polymer host mixed matrix membrane which can improved the CO₂/CH₄ selectivity.

CONCLUSION

In this study, hybrid mixed matrix membranes were produced using polyethersulfone (PES) as polymer matrix and carbon nanotubes as inorganic filler. The membrane performance was tested for CO₂ removal. The FESEM for the cross-sectional and surface area images of mixed

matrix membrane films indicated that the acid treatment can modify the surface of carbon nanotubes. Therefore, the carbon nanotubes was dispersed well in the polymer matrix. The surface ruptures are not occurred on the carbon nanotubes hybrid mixed matrix membrane might be due to the shape of carbon nanotubes appeared to be oblong. The smooth surface of carbon nanotubes might also help to enhance the adherence between the nanotubes and the host polymer. The PES-modified carbon nanotubes membranes had increased the permeability of carbon dioxide gas and the CO₂/CH₄ selectivity. The carbon nanotubes have been potentially as inorganic filler for mixed matrix membrane for the future CO₂ removal membrane application i.e. biogas purification, natural gas and flue gas purification membrane.

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Persian Abstract

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چکیده

اخیراً، بسیاری از پژوهشگران، استفاده از غشای ساختار مرکب را مورد بررسی قرار داده اند. فرآیندهای جداسازی بر اساس غشای ساختار مرکب، که متشکل از مواد معدنی مانند زئولیت و نانولوله های کربنی (CNTs) تعبیه شده در ساختار شبکه پلیمر می باشد که یکی از فن آوری های نوین بوده و بطور گسترده در نشریات جداسازی غشایی مورد بحث قرار گرفته است. مقاله حاضر، به منظور بررسی اثر اصلاح شیمیایی در سطح نانولوله های کربنی، بر عملکرد جداسازی گاز، از غشای ساختار مرکب انجام شده است. غشای ساختار مرکب متشکل از نانولوله های کربنی پلی اترسولفون (PES)، با استفاده از روش واژگونی فاز خشک/ تر، برای نانولوله های کربنی اصلاح شده و اصلاح نشده، قالب گیری شد. نانولوله های کربنی اصلاح شده، با تیمار اسیدی، به منظور نشان دادن زنجیره های PES، بر روی سطح نانولوله، بدست می آیند. نتایج حاصل از آنالیزهای FESEM، DSC و FTIR، نشان می دهد که تغییرات شیمیایی مورد نظر، بر روی سطح نانولوله های کربنی، صورت گرفته است. همچنین، در حالتی که در غشای ساختار مرکب PES، از نانولوله کربنی اصلاح نشده استفاده شود، شکاف هایی در محدوده ابعاد نانو، در فصل مشترک پلیمر و نانولوله های کربنی، ظاهر می گردد. در غشای ساختار مرکب نانولوله های کربنی اصلاح شده، خواص مکانیکی، بهره وری و خلوص مخلوط گازی را نسبت به PES و غشای ساختار مرکب حاصل از نانولوله کربنی اصلاح نشده، بهبود یافته است.
