

IMPROVEMENT MIXED MATRIX MEMBRANES PERFORMANCE OF MCM-41/ PSf FOR CO₂ SEPARATION USING SILANE COUPLING AGENT

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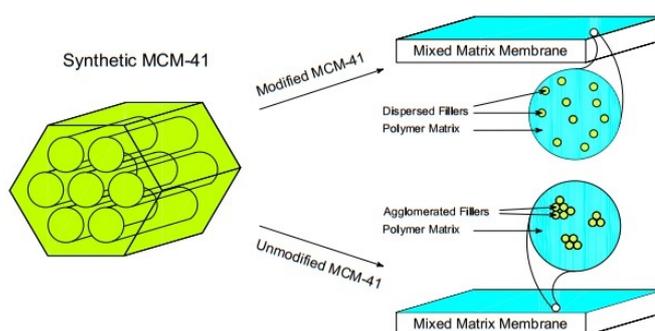
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For this research was fabricated a polysulfone (PSf)- MCM-41 mixed matrix membranes (MMMs) for separation of CO₂ from CH₄. For this purpose, the mesoporous MCM-41 particles synthesized by hydrothermal method. In order to improve particle dispersion and increase the compatibility and coupling between particle and polymer matrix, the surface of MCM-41 modified by 3-aminopropyltriethoxysilane (APTES). The synthesized and functionalized articles were characterized by SEM and FTIR analysis and it was shown that the surface of particles were successfully modified. The unmodified and modified particles were then used in values of 5, 10, 15 and 20 wt % in the polymer matrix and then FTIR and SEM analysis were used to study the synthesized membranes. Finally the gas separation performance including CO₂ and CH₄ permeability as well as CO₂/CH₄ selectivity of synthesized MMMs were investigated. The addition of any type of MCM-41 particles to the PSf matrix were increased the measured permeability, while selectivity showed a different trend depending on the presence or absence of the silane coupling agent. Generally, the addition of modified MCM-41 to the PSf matrix was improved the gas separation performance compared to other fabricated membranes.



INTRODUCTION

The separation of the CO₂ gas as an undesirable component to increase the heating value of the fuel is one of the general separation processes in the natural gas industry. In addition, CO₂ causes the corrosion of process equipment in the presence of water. Therefore, it is necessary to separate CO₂ from CH₄ and bringing it to an acceptable limit prior to transmission and distribution of natural gas. Different technologies are used to separate CO₂ in the industry, such as separation by chemical

solvents, physical solvents and membrane technology.¹⁻³

In the last two decades, membrane technology has been used for various separation. A membrane has the ability to selectively pass one component into a mixture and does not allow other components to pass through.⁴⁻⁶ The difference in permeability rate of gases is the basis of membrane processes for gas separation. Polymeric membranes have process properties including low energy consumption, high transport properties, low fixed and current costs. Robeson showed that there is a

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reverse relation between permeability and selectivity of polymeric membranes. To overcome this challenge in the separation properties of neat polymeric membranes, the concept of MMMs was presented. In the MMMs, the special properties of the separation of minerals with mechanical properties and economical cost of polymeric materials have been mixed.⁷⁻¹² The minerals used in the synthesis of MMMs as filler have a unique structure in terms of chemical surface and high mechanical resistance and it is expected to increase the properties of polymer separation and mechanical and thermal resistance when added to the polymer matrix. The mesoporous MCM-41 particles has attracted much attention as a member of the M41S family (MCM-41, MCM-48 and MCM-50) due to the high surface area, regular porous structure, small pore diameter and scattering.¹³ In addition, polymer chains can penetrate into the pores of different fillers and increase the adhesion between polymer and nanoparticles by blocking the partial pores.¹⁴ Reid *et al.* were the first research group to study the MMM consisting of PSf and MCM-41 for gas separation, so that the mixture of MCM-41 with PSf increased permeability significantly while selectivity didn't change much.^{15,16} Kim *et al.* increased the gas permeability of PSf by incorporation of MCM-48 nanoparticle, while selectivity of the membrane was not significantly altered.^{17,18} Most of the MMMs show higher gas permeability as well as enhanced or identical selectivity in comparison with neat membranes.¹⁹⁻²³

Although it is expected that by adding nanoparticles to the polymer structure, the separation properties of gas in the MMM can be improved, but sometimes fabrication of MMMs can lead to non-ideal effects such as agglomeration of nanoparticles, formation of surface voids around the nanoparticles, blockage of the free space around the nanoparticles and the rigidity of the polymer layer around the nanoparticles. The agglomeration of nanoparticles and formation of surface voids around the nanoparticle in the MMM results in the formation of non-selective voids in the membrane which these non-selective voids are formed due to the weak compatibility between the polymer and the nanoparticles and they are challenged the gas separation performance.^{24,25} Tantekin-Ersolmaz *et al.* in their study reported that the MMM consists of glassy polymers and zeolites causes an increase in separation. however, the fabrication of MMMs using glassy polymers causes the formation of voids between the polymer and the zeolite, thus reducing the MMM performance in comparison with neat polymer.²⁶ It

is usually used to prevent agglomeration of nanoparticles and increase the adhesion of nanoparticles to polymer matrix their surface is modified. Nanoparticles surface modification both organic and inorganic materials in order to change their physical and chemical properties is done. The silane coupling agents are the most prominent class of organic compounds that can be used for modification.^{27,28} The choice of type of silane coupling agent is based on the type and structure of the polymer network and the type of the existing interaction.²⁹ The appropriate silane selection for the surface modification of the nanoparticles at the time of fabricating the membrane increases the adhesion between the silica surface and the polymer network.³⁰ Organosilanes act as a bridge between the inorganic nanoparticles and the polymer network and significantly increase adhesion between them.³¹ Shimizu *et al.* reported that the addition of functionalized mesoporous SBA-15 nanoparticles by aminosilane is effective on the selectivity of CO₂/CH₄.³²

The aim of this study was to fabricate neat PSf membrane and MMMs containing PSf and modified and unmodified MCM-41 for separation of CO₂ from CH₄. In this work, APTES silane coupling agent without solvent was used to modify the surface of MCM-41 (solvent free method). The MMMs were prepared by adding the MCM-41 at a specific weight percent to the polymer solutions for fabricate nanocomposite membranes containing 5, 10, 15 and 20 weight percent MCM-41. Modified and unmodified particles and fabricated membranes were characterized by different analysis. Finally, the performance of different membranes in the separation of CO₂ from CH₄ such as permeability and selectivity was evaluated.

EXPERIMENTAL

Material

Cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), sodium hydroxide (NaOH), tetrahydrofuran (THF) and APTES were purchased from merck. Anhydrous toluene was purchased from Sigma Chemical Co., Iran. Moreover, polysulfone (Udel P-1700 grade), a glassy polymer with a glass transition temperature (T_g) of 185°C, was obtained from Amoco.

Synthesis of MCM-41 particles

In this research, hydrothermal method was used to achieve the MCM-41 particles with uniform pore size distribution. In this method, an aqueous micellar solution containing 1 g of CTAB surfactant, 0.28 g of NaOH, and 480 mL of deionized water was prepared under stirring for 1 h. Then, 5 mL of TEOS, as a silica source, was slowly added to the solution at 80°C in an oil bath to form a white slurry solution. After 2 h stirring

(500 rpm), the slurry was transferred to a glass container and was left for 24 h to be completely transformed. The slurry was filtered using a ceramic filter and washed many times with deionized water until the filtrate became neutral. Then, the resulting precipitate was products was dried at ambient temperature. Finally, the obtained powder was calcined at 550°C in the air for 6 h to remove the surfactant.^{33,34}

Modification of MCM- 41 particles without using solvent

The silane coupling agent acts as an interface between a mineral (MCM-41 particle) and an organic matter (PSf) as two different materials. In this method for surface modification of particles using silane, functional groups without using solvent in the particles are created. A mixture of 0.5 g synthesized MCM-41 and 10 ml APTES at 68°C was refluxed under stirring and nitrogen atmosphere for 48 h. After cooling, the mixture was filtered and washed with ethanol. Eventually the excess amine was removed by soxhlet-extraction using methylene chloride (CH₂Cl₂) for 10 h and the amine modified MCM-41 particles were dried for 6 h at room temperature under vacuum.

Fabrication of membranes

All of the membranes were fabricated using the solution casting method. Before preparation of the membranes, PSf was degased at 80°C for 8 h under vacuum to remove absorbed moisture. For preparing the neat membrane with 10 wt % PSf, 0.5 g PSf was added to the proportional value of THF and the mixture was stirred for 4 h to produce a uniform solution. Then the solution was cast onto a glass plate and for solvent evaporation, it was placed at 40°C for 24 h. The remaining solvent in the prepared membrane was evaporated in a vacuum oven at 85°C for 4 h.

For fabrication of the MMMs in the first step, due to the presence of different amount of particles in the polymer matrix (5, 10, 15 and 20 wt), the amount of each of modified and unmodified MCM-41 was dried in a vacuum oven. Then each of the fillers was added to 3 g of THF and the mixture was stirred for 10 h and to increase dispersion was sonicated for 20 minute. The process of stirring and sonicating were repeated twice. At the same time, a homogeneous solution containing PSf and THF was stirred in another container. Then 4-5 drops of this solution were added to the suspension and this suspension was stirred and sonicated for 20 minute again in order to cover the surface of the particles. After that, the remainder of the polymeric solution was added to the suspension and this suspension was stirred and sonicated to prevent formation of particle agglomerates. Then, the mixture was stirred for 4 h at room temperature and was sonicated for 10 minute to remove any gas bubbles before casting. Final casting on a glass plate is similar to that of neat PSf membrane.

In this study, three groups of membranes, including neat PSf membrane, MMMs consisting of PSf and different weight percents (5, 10, 15, 20%) of unmodified and APTES-modified MCM-41 were prepared and are labelled a PSf, PSf-UMO-Mx and PSf-AP-Mx (x indicates the weight percentage of particles). A schematic of the different types of fabricated membranes is shown in Figure 1.

Characterization

Fourier transform infrared (FTIR) Spectroscopy was done by using THERMO AVATAR spectrometer in the range of 400-4000 cm⁻¹ to characterize the functional groups of the particles. The morphology of unmodified and modified MCM-41 particles and membranes was investigated using a MIRRA 3 TESCAN scanning electron microscope (SEM). Membranes were broken under liquid nitrogen and sputter coated with gold using Cressington HR208 (UK) high resolution sputter coater. X-ray diffraction (XRD) patterns were determined using X'Pert Pro, analytical X-ray diffractometer. The results were recorded using Cu K α radiation ($\lambda = 1.54\text{\AA}$) in the 2 θ range of 10–90° for neat membrane and MMMs.

Gas permeation measurements

After fabrication of PSf membrane and MMMs, these membranes were tested for gas permeability to CH₄ and CO₂ gases with a purity of 99.99%, respectively. The fabricated membranes were tested in a pure gas system. The permeation measurements of CH₄ and CO₂ were performed at pressure of 8 bar and room temperature for all membranes. In this study, constant pressure test device is used to study gas permeability into the membrane and recording the flow rate of gas. The permeability test apparatus consists of a gas permeability cell that the membrane is located into and one side of it is exposed to gas feed. The pressure on the feed side is regulated by the regulator and is measured by the pressure gauge and the downstream pressure is the ambient pressure, and changes in the volume of gas passing through the membrane is recorded. The permeability of gas *i*, P_i , in membrane is obtained with the following equation:

$$P_i = \frac{l}{A\Delta P} \frac{dV_i}{dt} \quad (1)$$

where P_i is gas permeability of *i* in barrer, V_i is volume of gas displaced in the flow meter of soap bubble or volume of gas permeation in the membrane according to the cubic centimeter, A is the effective surface of the membrane equal to 15.9 square centimeters, l is the membrane thickness in cm, t is the time interval of bubble movement in the column in second and ΔP is the pressure drop across the membrane in cmHg. In this study the gas permeability was investigated at 8 atm.

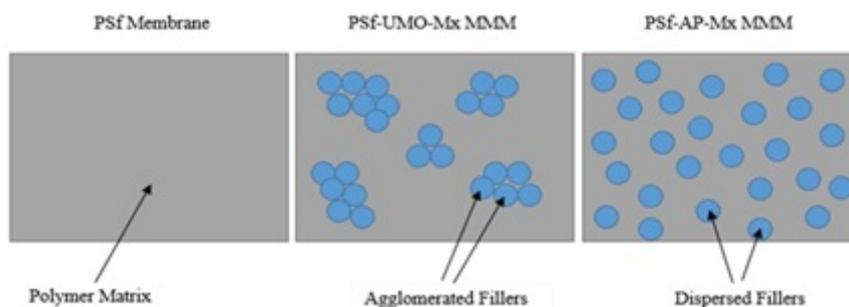


Fig. 1 – A schematic of the different types of fabricated membranes.

The ideal selectivity of gases, $\alpha_{i/j}$, for each membrane is obtained with the following Equation:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

where $\alpha_{i/j}$ is the ideal selectivity of gas *i* to *j* and P_i and P_j are the permeability of the gases *i* and *j* respectively.

RESULTS AND DISCUSSION

Characterization results of silica MCM-41

The morphology of silica mesoporous particles was investigated by SEM analysis as shown in Figure 2. This Figure shows the micrographs of unmodified MCM-41 and APTES-modified MCM-41 particles, respectively, which are spherical shape and have a particle diameter between 200 and 650 nm. As can be seen, the MCM-41 particles have not undergone structural and morphological changes after modification, and their structure has been preserved.

The Fourier transform infrared (FTIR) spectrometer of unmodified and modified MCM-41 particles in the range of 4000-400 cm^{-1} under ambient conditions is shown in Figure 3. For the unmodified MCM-41, the peaks observed in region 3402 cm^{-1} belong to the O-H stretching vibrations of the water molecules adsorbed on its surface as well as the hydroxyl silanol Si-OH groups. The peak observed in 1626 cm^{-1} also belongs to the vibrations of H₂O molecules trapped in the lattice. The main feature of MCM-41 is the presence of a silicate network. This characteristic is observed by the peaks of 460 cm^{-1} , 950 cm^{-1} and 1084 cm^{-1} , which belong to the Si-O-Si, Si-OH and Si-O

silicate groups, respectively. After the MCM-41 particles became functional without the use of solvent, a new peak appeared in the 2932 cm^{-1} area. This peak belong to the vibrations of C-H group, which is caused by the substituent propyl group of APTES. The changes observed in the 1480 cm^{-1} region also indicate changes in amine bonds that occur after functionalization. Amination also changes the appearance of the peak in the 3402 cm^{-1} . These results indicate that particles modification has been successfully performed by APTES.

Characterization results of Mixed Matrix Membranes

In this study, SEM analysis was used to evaluate the dispersion quality of MCM-41 particles in the PSf matrix. SEM micrographs of the cross section for PSf-UMO-M10 and PSf-AP-M10 MMMs are shown in Figure 4. Figure 4 (a1) and (a2) shows that unmodified MCM-41 particles have accumulated in the PSf matrix and that undesirable voids have formed between the mineral particles and the PSf matrix. The formation of these undesirable and non-selective voids is due to the weak bond between the polymer and the mineral fillers and also the formation of hydrogen bonds between the silanol groups of MCM-41 which leads to a decrease in the selectivity and mechanical properties of the MMM. While in the MMM with APTES-modified particles, it shows a more uniform dispersion compared to the unmodified particles and no definite void is seen between the polymer and the filler (Figure 4 (b1) and ((b2))).

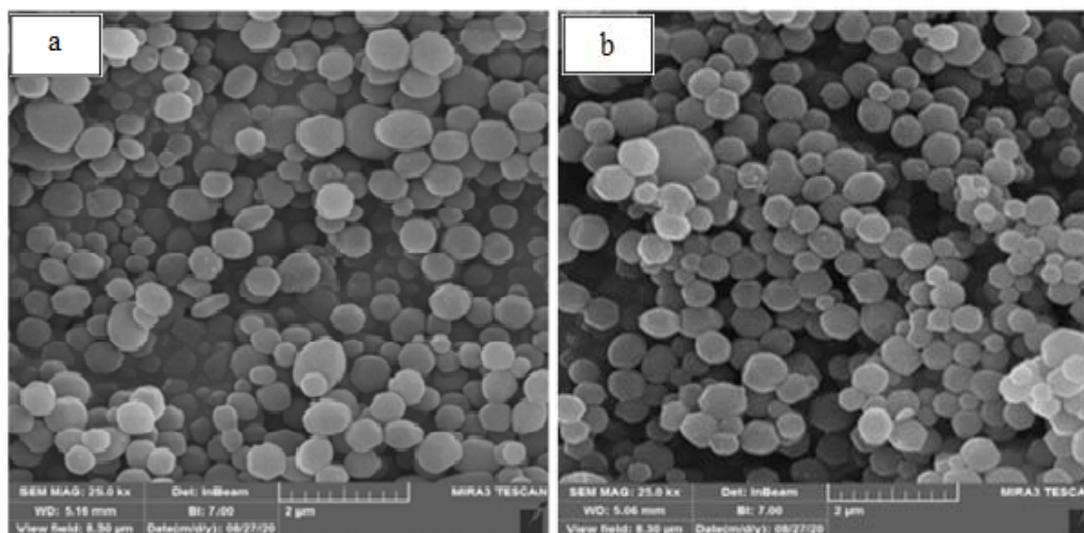


Fig. 2 – SEM image of (a) unmodified and (b) APTES modified MCM-41.

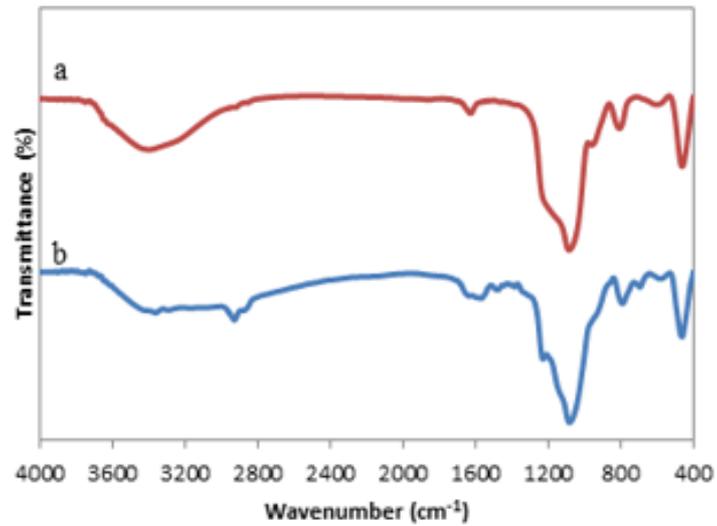


Fig. 3 – FTIR spectra for the (a) unmodified and (b) APTES modified MCM-41.

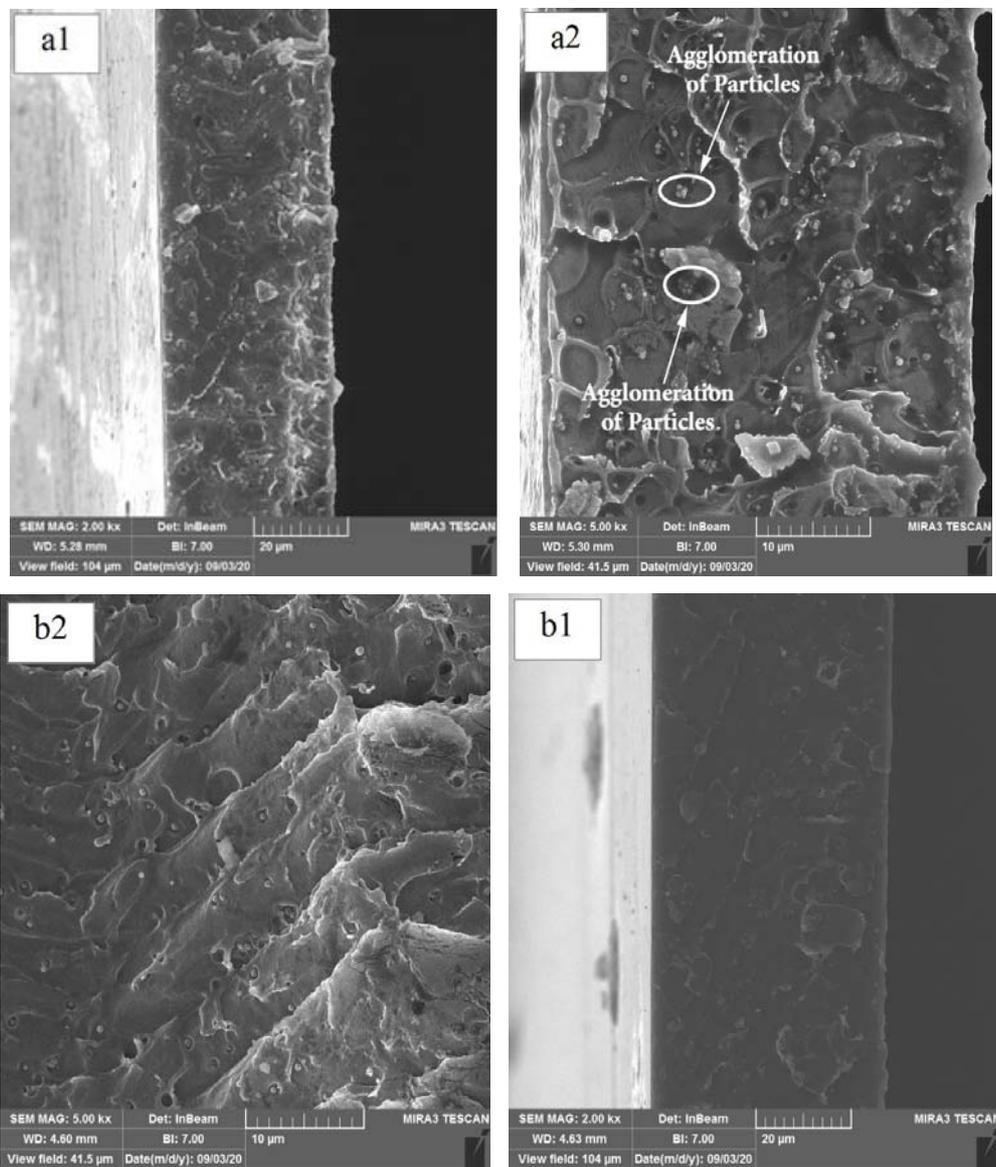


Fig. 4 – Cross-sectional SEM images for (a1) PSf-UMO-M10, (a2) details of (a1), (b1) PSf-AP-M10, (b2) details of (b1).

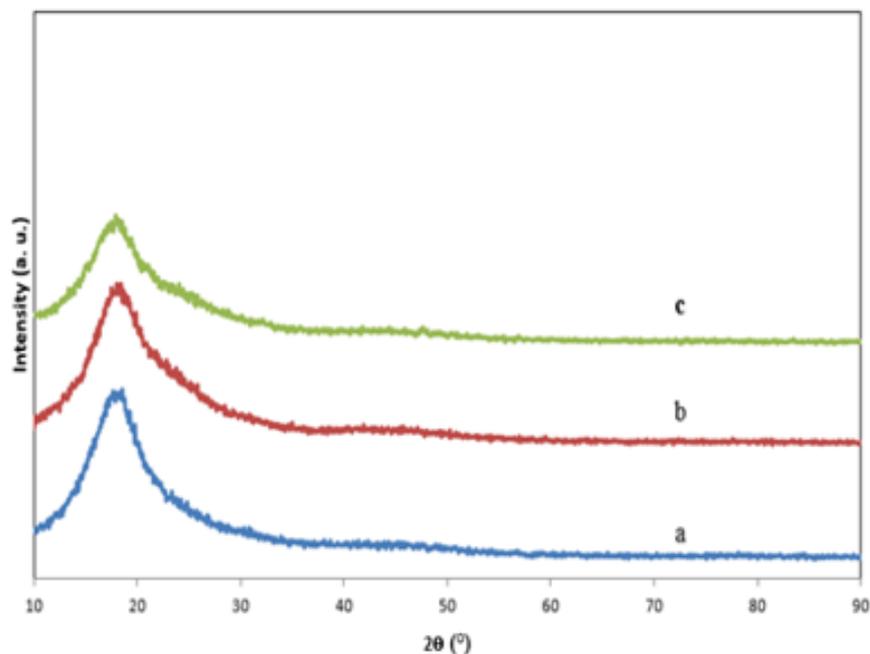


Fig. 5 – XRD patterns for (a) The neat PSf, (b) PSf-UMO-M10 and (c) PSf-AP-M10.

The X-ray diffraction (XRD) diagram for PSf membrane and PSf-UMO-M10 and PSf-AP-M10 MMMs is shown in Figure 5. The PSf membrane is amorphous and lacks a crystalline structure and shows a sharp peak around $2\theta=18^\circ$. The second wide peak is around $2\theta=44^\circ$. As can be seen in the Figure 5, all diagrams of composite membranes show a similar diffraction pattern that originates from the amorphous structure of the polymer. Therefore, the addition of MCM-41 did not change the diffraction pattern of the neat PSf membrane, and the pattern characteristic and amorphous nature of the membrane structure were retained.

Gas separation results

CO_2 and CH_4 permeability were measured in PSf membrane and PSf-modified and unmodified MCM-41 MMMs at room temperature and 8 bar pressure. The measured permeability for CO_2 and CH_4 gases and the calculated ideal selectivity of CO_2/CH_4 for different membranes prepared are given in Table 1. As can be seen in Table 1, CO_2 has a higher permeability than CH_4 in the polymer matrix, the main reason being the lower kinetic diameter of CO_2 than CH_4 (kinetic diameters of CO_2 and CH_4 are 3.3 Å and 3.8 Å, respectively). Also, the condensability temperature of CO_2 is higher than CH_4 , and the interactions of CO_2 with the polymer chain are higher than CH_4 . Therefore,

CO_2 has more solubility and therefore more permeability than CH_4 .^{35,36}

In this study, as can be seen in Table 1, Regardless of the particles type, adding MCM-41 into PSf matrix increases the gas permeability of the MMMs compared to the neat PSf, but the addition of unmodified particles led to a significant enhancement of permeabilities even compared to other MMMs with modified particles. In PSf-unmodified MCM-41 MMM by adding 20 wt% of particle to PSf, the CO_2 permeability increased from 5.8 barrer for PSf membrane to 12.46 barrer, i.e. CO_2 permeability increased by 114.83%. Similarly, the addition of 20 wt% of particle to PSf increased the CH_4 permeability from 0.3 barrer for PSf membrane to 0.65 barrer, indicating a 116.67% increase in CH_4 permeability. The results show that in MMMs fabricated of PSf and unmodified MCM-41, selectivity was increased to a concentration of 10 wt% of MCM-41 and for higher concentrations of MCM-41 was reduced selectivity. It means that the ideal selectivity of CO_2/CH_4 was increased from 19.33 for PSf membrane to 20.69 for PSf-UMO-M10 MMM and then the selectivity was reduced for PSf-UMO-M20 MMM and reached to 19.17.

This decrease in selectivity is due to the weak interfacial tension of the particle-polymer as well as the agglomeration of particles in the polymer matrix. In the MMMs consisting of mineral particles dispersed in a polymer matrix, the bond

between the two materials plays an important role in the performance of these membranes. Therefore, in order to increase the adsorption capacity of CO₂ by the membrane, the surface of silica MCM-41 particles was modified before being placed in the polymer matrix by APTES and its effect on the separation performance of PSf-MCM-41 MMM was investigated. For APTES-modified particles in the PSf matrix, the polar groups of the aminopropyl bond interact with the polar sulfone groups to form a new hydrogen bond. Therefore, the addition of modified MCM-41 particles to PSf causes the particles to be homogeneously dispersed in the polymer structure and produce a MMM without defects.

As is observed from the separation results for PSf-modified MCM-41 MMMs, the permeability for CO₂ and CH₄ was increased with adding the amount of particles loaded in PSf matrix (Table 1). However, the use of functionalized MCM-41 increased the selectivity due to the proper performance of APTES to reduce agglomeration of particles and increase the adhesion and compatibility of particles with PSf matrix. By comparing the permeability of PSf-modified MCM-41 MMMs with PSf membrane, as expected, an increase in permeability is observed. It is also observed that the selectivity of the MMMs with modified particles is significantly increased compared to other fabricated membranes, so that in the PSf-UMO-M20 MMM, selectivity of 19.17 was

achieved, however for the PSf-AP-M20 MMM, the selectivity was obtained 24.2.

CONCLUSIONS

In this study, silica MCM-41 particles were prepared by hydrothermal method and added to the PSf matrix to fabricate MMMs. Addition of unmodified and modified MCM-41 to the PSf matrix increased the permeability of all fabricated membranes compared to PSf membrane, but due to the presence or absence of silane coupling agent, selectivity showed a different trend. In MMMs with unmodified particles, the ideal selectivity did not change much due to the low quality of particle dispersion and the formation of non-selective voids. In order to prevent the agglomeration of MCM-41 particles in the polymer matrix, these particles were modified using APTES without solvent. The results of particles FTIR analysis showed that particles modification by silane was successfully performed. The morphology of the membranes was investigated by SEM analysis, which showed an increase in the dispersion of modified particles in PSf compared to unmodified particles. As a result, MMMs fabricated with modified MCM-41 particles, in addition to increasing permeability, caused a significant increase in the selectivity of CO₂/CH₄.

Table 1

permeabilities (Barrer) and selectivities of CO₂ and CH₄ through the neat PSf, unmodified and modified MCM-41 MMMs at 8 bar and room temperature

Membrane	CO ₂	CH ₄	CO ₂ /CH ₄
PSf	5.80	0.30	19.33
PSf-UMO-M5	8.05	0.39	20.64
PSf-UMO-M10	9.93	0.48	20.69
PSf-UMO-M15	11.14	0.57	19.54
PSf-UMO-M20	12.46	0.65	19.17
PSf-AP-M5	7.68	0.39	19.69
PSf-AP-M10	9.49	0.43	22.07
PSf-AP-M20	10.92	0.47	23.23
PSf-AP-M20	12.10	0.50	24.20

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