Synergistic effect of binary fillers (MCM-41/C20) hybrid membrane for CO_2/CH_4 separation

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Abstract. A novel binary fillers hybrid membrane was formed by incorporating Mobil Composition of Matter-41 (MCM-41) nanoparticles and Cloisite 20 nanoclay layers (C20) into polysulfone (PSf) polymer matrix in order to resolve common agglomerations issue in hybrid membrane and to enhance gas separation performance. Enhanced dispersion degree of MCM-41 nanoparticles and enhanced exfoliation of C20 layers were achieved in the binary fillers hybrid membrane. The resultant membrane showed excellent gas separation performance compared to pristine PSf membrane and single filler hybrid membrane. A 25% improvement in CO_2/CH_4 ideal selectivity (α = 28.7) was observed in the gas permeation of binary fillers hybrid membrane without compromising CO_2 permeability (P_{CO_2} = 6).

1. Introduction

In recent decades, membrane technology has successfully emerged as one of the most important separation methods in industries [1]. Hybrid membrane (HM), which consists of inorganic fillers dispersed in polymer matrix, is of great interest to scientists due to its excellent mechanical and thermal properties [2]. However, achieving uniform dispersion and distribution of inorganic fillers in polymer matrix is often challenging as inorganic particles with identical nature tends to agglomerate and cause poor dispersion, leading to uneven properties of membrane [3]. Furthermore, it is often noticed that the resultant hybrid membranes showed either improvement in terms of gas permeability or selectivity, but not both [4-6]. An ideal membrane should possess high gas permeability and selectivity, hence this led to the development of binary fillers HM. Binary fillers dispersion method was recently introduced to homogeneously disperse nanoparticles in HM and to enhance overall membrane gas separation performance.

Zornoza et al. investigated the synergistic effect of binary fillers by combining metal-organic framework (MOF) and silicalite-1 (S1C) into polysulfone (PSf) for gas separation [3]. Two MOFs, ZIF-8 and HKUST-1, with partially organic nature were also incorporated, since they ensure the chemical affinity with polymer matrix. Due to the increase in polymer matrix free volume caused by inorganic filler disruption, 88% increment in gas permeability was achieved. Furthermore, the combination of HKUST-1/S1C shows optimum performance with 50% improvement in selectivity compared to single filler HM. This is due to enhancement in particles dispersion as particles of different nature were incorporated into the matrix. Recently, Li *et al*. adapted the binary fillers technology from waste water treatment by combining carbon nanotube (CNT) and graphene oxide (GO) to form HM for CO_2/CH_4 separation [7]. They found that HM with 5wt% of CNT and 5wt% of

GO (Matrimid® CNT/GO-5/5) gives highest gas permeability and selectivity. The excellent separation performance of Matrimid® CNT/GO-5/5 was attributed to homogeneous dispersion of CNT and GO in the polymer matrix as well as good adhesion between fillers and polymer. GO which is in layered form, possesses strong steric effect and prevented CNT from agglomeration. The well dispersed CNT, on the other hand, inhibited the stacking of GO nanolayer in the membrane. In another study, Mahdavi and Moradi-Garakani [8] also discovered improved gas separation performance through incorporation of MOF and fumed silica in polyethersulfone HM. However, minimal work has been done to correlate the dispersion degree to gas separation performance.

In the present work, a novel binary fillers HM was formed by incorporating mesoporous silica nanoparticles (Mobil Composition of Matter-41, MCM-41) and layered-silicate (Cloisite 20, C20) into polysulfone (PSf) polymer matrix. The objective of this research was to enhance fillers dispersion degree and CO_2/CH_4 gas separation performance. The effects of binary fillers on MCM-41 nanoparticles dispersion, exfoliations of C20 nanoclay layers, and gas separation performance were investigated through comparison with pristine and respective single filler HM. Furthermore, image processing toolbox from MATLAB was employed to quantitatively analyse the blob area fraction (agglomerates area fraction) and size of agglomerates (L_a) for particles dispersion degree study.

2. Experimental Method

MCM-41, C20 and PSf loadings were pre-determined and optimized at 0.5 wt%, 1 wt% and 26 wt%, respectively. C20 was first dispersed in tetrahydrofuran (THF) for 30 minutes using IKA T25 Digital Ultra-Turrax disperser. MCM-41 was slowly added and dispersed in the mixture for another 30 minutes. PSf was added batch-wise into the mixture and stirred until the pellets were completely dissolved. The solution was cast on a clean and flat glass plate using casting knife with 150 μm gap setting. The resultant film was placed in a covered tray to slow evaporation. The formed membrane was dried for 3 days at room temperature. Pristine PSf membrane and single filler HM at similar loadings (PSf/MCM-41 and PSf/C20) were fabricated via the same method. Images of the membrane were obtained using scanning electron microscope (SEM, Hitachi TM3030) and transmission electron microscope (TEM, FEI Tecnai F20S). The blob area fraction and size of largest agglomerates (L_a) of resultant HM were estimated through developed MATLAB coding. Gas permeation properties of resultant membranes with 1.8 cm^2 effective area, were measured using CO_2 and CH_4 (99.995% purity) at feed side pressure of 8 bar. Permeability and ideal selectivity of gases were calculated based on previously published equations [9, 10].

3. Results and Discussion

3.1. Effect of binary fillers on nanoparticles agglomeration

Blob area fraction of nanoparticles (MCM-41 and C20) in resultant binary fillers HM was obtained and compared with the respective single filler HM, as depicted in figure 1. It was noticed that binary fillers HM demonstrated the smallest blob area fraction, which indicates that better dispersion and distribution of nanoparticles were obtained. A small blob area fraction also suggested that lesser agglomerates were formed in the HM. In addition, L_a of binary fillers HM was estimated from SEM images. It was discovered that the L_a of binary fillers HM was the smallest, as shown in figure 2. This again verifies that the dispersion and distribution of nanoparticles were enhanced in binary fillers HM. This improvement can be attributed to the low cohesive strength of nanoparticles. According to Khare and Burris [11], nanoparticles of the same surface nature (or the same type of nanoparticles) possess strong cohesive strength and weak adhesive force. These particles usually exhibit high specific surface area and energy, which caused them to "stick" to one another and were difficult to separate. On the contrary, nanoparticles of different nature demonstrated an antagonistic effect and caused them to separate from each other. Furthermore, the C20 nanoclay layers in binary fillers HM acted as a sheet barrier that hindered the agglomeration of MCM-41. This steric hindrance effect caused MCM-41 nanoparticles to disperse well in PSf matrix, hence reduced the size of agglomerates. On the other

hand, the well dispersed MCM-41 nanoparticles had also inhibited the restacking of C20 nanoclay layers, resulting in increased basal spacing of the layers, as illustrated in figure 3. Compared to C20 single filler HM, which demonstrated a basal spacing of 17.9 nm, binary fillers HM displayed increased basal spacing at 28.55 nm. Thus, it can be concluded that enhancement in nanoparticles dispersion and clay exfoliations were achieved by incorporating binary fillers in HM.

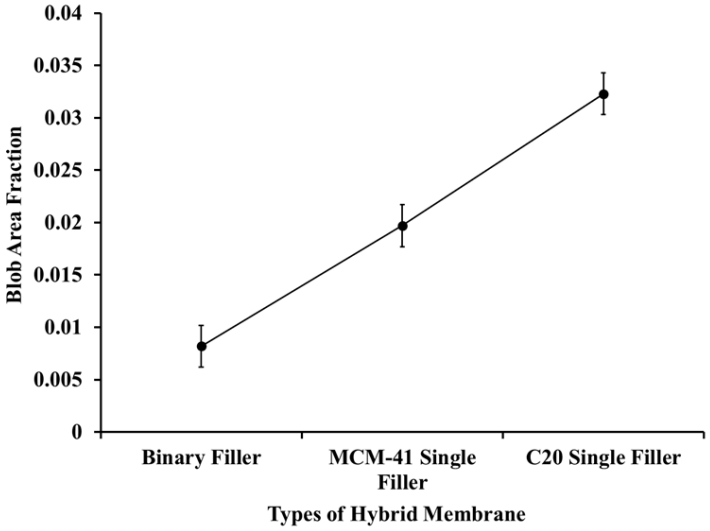

Figure 1. Blob area fraction for different types of HM.

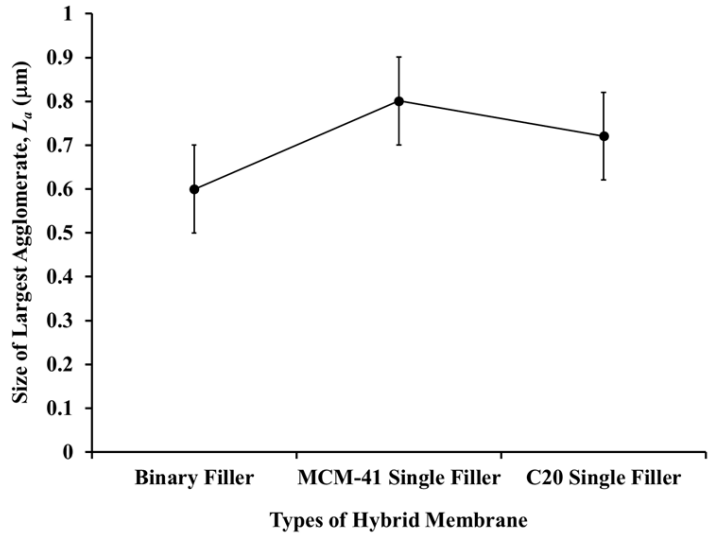

Figure 2. Size of largest agglomerates (L_a) for different types of HM.

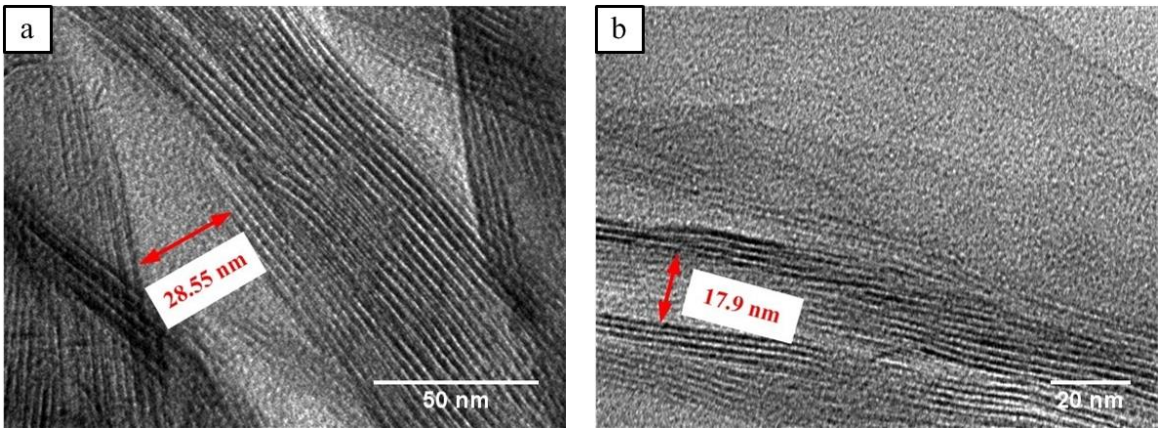

Figure 3. TEM micrographs of (a) binary fillers HM and (b) C20 single filler.

3.2. Effect of binary fillers on gas separation performance

The CO_2/CH_4 ideal selectivity against CO_2 permeability of resultant membranes were plotted, as illustrated in figure 4. Binary fillers HM demonstrated improved gas separation performance. The resultant binary fillers HM showed 25% improvement in CO_2/CH_4 selectivity (α = 28.7) compared to pristine PSf (α = 22.9) membrane without compromising the gas permeability (P_{CO_2} = 6). This increase in selectivity can be attributed to the well exfoliated non-porous C20 nanoclay layers. The non-porous structure of C20 acts as a gas barrier that restricted the direct diffusion of gases through the membrane by forcing gases to diffuse through tortuous route created by the exfoliated layers [12, 13]. CH_4 that has larger kinetic diameter ($d_k(CH_4)$= 3.8 Å) than CO_2 ($d_k(CO_2)$= 3.3 Å) experienced higher restriction in the diffusion through the membrane with well exfoliated and randomly oriented C20 nanoclay layers. Reduction in permeability of CH_4 caused an increase in CO_2/CH_4 selectivity of the membrane. In addition, the mesoporous structure of MCM-41 facilitated gas permeation by allowing gases to pass through the pores with minimal resistance. Thus, a reduction in CO_2 permeability was not observed even with the incorporation of C20 in binary fillers HM. Besides, it was also interesting to note that MCM-41 single filler HM demonstrated highest CO_2 permeability (P_{CO_2} = 7.5) and lowest CO_2/CH_4 selectivity (α = 22.1) among all the membranes. This could be due to the formation of large MCM-41 mesoporous agglomerate in MCM-41 single filler HM, as shown in figure 2. The mesoporous structure of MCM-41 agglomerates allow both CO_2 and CH_4 diffuse through the pores with minimal resistance, hence, low CO_2/CH_4 selectivity was observed. In contrast, MCM-41 agglomerates were reduced in binary fillers HM. Thus, reduction in CO_2/CH_4 selectivity was not observed in binary fillers HM. On the other hand, PSf/C20 single filler HM showed increase in CO_2/CH_4 selectivity (α = 27.7) but decrease in the permeability of CO_2 (P_{CO_2} = 4.5) compared to pristine PSf membrane due to the tortuous path created by the exfoliated C20 nanoclay layers. However, the decrease in permeability of CO_2 was compensated by the introduction of MCM-41 in the binary fillers HM. Thus, this proved that the synergistic incorporation of binary fillers in the fabrication of HM enhanced the gas separation performance.

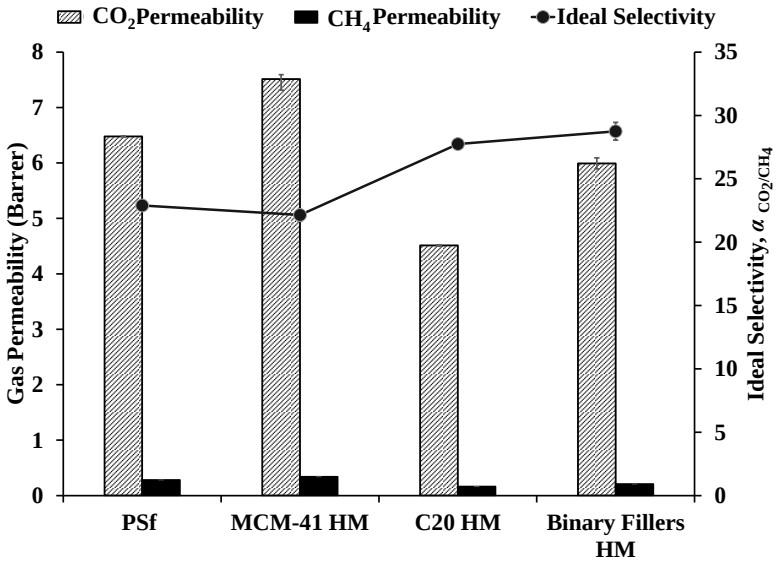

Figure 4. CO_2 permeability and CO_2/CH_4 ideal selectivity versus types of membrane

4. Conclusion

Synergistic incorporation of binary fillers in the fabrication of HM enhanced MCM-41 nanoparticles' dispersion, C20 nanoclay layers exfoliation and gas separation performance. MCM-41 nanoparticles were well dispersed in binary fillers HM due to the steric hindrance effect caused by exfoliated C20 nanoclay layers. On the other hand, the restacking of C20 nanoclay layers was inhibited by the well dispersed MCM-41 nanoparticles. 25% improvement in CO_2/CH_4 ideal selectivity was achieved by the binary fillers HM without compromising CO_2 permeability.

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