Improving Gas Separation Performance of Poly(vinylidene fluoride) Based Mixed Matrix Membranes Containing Metal–Organic Frameworks by Chemical Modification

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ABSTRACT: In this study, poly(vinylidene fluoride) (PVDF) was modified by a mixture of KOH and KMNO$_4$ in order to effect HF elimination. During this reaction, some functional groups were created in the PVDF structure. The metal–organic frameworks, MIL-53(Al) and NH$_2$-MIL-35(Al), were embedded in modified PVDF (M-PVDF) to fabricate mixed matrix membranes (MMMs). Different characterization techniques such as FT-IR, XRD, SEM, DSC, TGA, and contact angle tests have been implemented to identify the prepared membranes. Pure and mixed (1:1) CO$_2$ and CH$_4$ were used to test gas separation performance of MMMS. CO$_2$ permeance was increased for pure M-PVDF membrane compared with the pristine PVDF by 31.2%. Upon 10 wt % loading of MIL-53(Al) and NH$_2$-MIL-35(Al) in M-PVDF, CO$_2$ permeability increased 104.33% and 80.02% relative to the unfilled M-PVDF. The highest CO$_2$/CH$_4$ ideal selectivity and separation factor of 43.9 and 42.65, respectively, were reported for NH$_2$-MIL-35(Al)/M-PVDF with 10 wt % loading. These improvements could be attributed to the breathing effect of MOFs, created polar moieties in PVDF through the modification, and hydrogen bonding interactions between the MOFs and the polymer.

1. INTRODUCTION

Over the last two decades, different inorganic filler particles have been dispersed in polymer matrices to fabricate the so-called mixed matrix membranes (MMMs), first reported by Zimmerman. In the gas separation processes, MMMS are promising methods to overcome the main constraint of polymeric membranes, which is the trade-off between permeability and selectivity. MMMs benefit of the superior gas transport properties afforded by inorganic fillers with the ease of fabrication and optimal mechanical properties of polymer matrices. Appropriate choice of polymer and filler is the most important challenge for which researchers are seeking solutions. Gas transport properties of MMMs strongly depend on the filler gas property and polymer–particle interface morphology. Nonselective voids, rigidification of polymer chains around particles, and partial blocking of particle pores by polymer are the most common morphologies that happen at the interface region. Low compatibility between polymer and filler can result in formation of nonselective voids at the interfacial region. Gas molecules are allowed to pass through such nonselective voids with no distinct selectivity. Consequently, the gas selectivity performance of whole membrane would be reduced. Inhibition of polymer chain mobility at the interface region creates chain rigidification morphology in MMMs. Chain rigidification affects the membrane separation performance in a different way compared with the nonselective voids. Partial blockage of the filler pores by penetration of polymer chains can impress interfacial morphology. If reduced pore size caused by partial pore blocking is appropriate to induce the molecular sieving mechanism, this morphology can help to improve gas separation behavior of membrane.

In addition, using fillers with appropriate surface functional groups and tendency toward some gases is another important factor that should be considered in MMM fabrication. Various families of fillers, such as zeolites, carbon molecular sieves, inorganic oxides, carbon nanotubes, carbon nanofiber, mesoporous silica, fullerenes, modified clay, and metal–organic frameworks (MOFs), have been utilized to incorporate into polymers. Recently MOFs have attracted attention of many researchers in MMM preparation since they constitute a transition metal complex or cluster and a polyfunctional organic linker. In principle, organic ligands with many different types of functionalities interact with polymer chains pretty well. Thus, formation of a nonselective void at the polymer–MOF interface, which deteriorates membrane gas separation performance, can be prevented. Moreover, MOFs can be prepared under moderate conditions and possess considerable characteristics such as large inner surface area, tunable pore size, uniform pore size distribution, controlled porosity, various topologies, flexibility in their chemical composition, and affinity toward certain gases.

Different studies were done to investigate the effect of Al based MOFs on performance of MMMs. The effect of NH$_2$-MIL-53 in 6FAD–4,4′-diamino diphenyl ether (ODA) polyimide for gas separation process was investigated by Chen et al. The MMMs with 32 wt % MOF showed high ideal selectivity of 77 and consequently high separation factor of 53. These results indicated the great adhesion between the polymer and NH$_2$-MIL-53 particles due to the hydrogen bonding interactions of NH$_2$ groups and polyimide.

The NH$_2$-MIL-53 synthesized by microwave heating was embedded in a polysulfone (PSF, Udels P-3500) matrix to...
examine CO2/CH4 separation. Fabricating an MMM with high filler up to 40 wt % loading was possible due to the strong matching of NH2-MIL-53 with PSF. Optimal loading of 25 wt % of MOF increased CO2/CH4 selectivity from 25 for MOF-free PSF to 46 approximately.21

Basu et al. in the study of mixed-matrix membranes comprising MOFs reported that MIL-53(Al) had higher selectivity for CO2 over CH4 than ZIF-8 in Matrimid matrix. The superior gas separation behavior was due to the strong CO2 interaction with the hydroxyl groups of the MIL-53(Al) and breathing mechanism of MIL-53(Al) in the presence of CO2.20

Chen et al. explored the nanosized amino-functionalized MOF, NH2-MIL-53, with two commercial polyimides (Matrimid 5218 and Ultem 1000) for gas separation. Matrimid/NH2-MIL-53 MMM showed high permeability for both CO2 and CH4 gases and relatively low CO2/CH4 selectivity compared with the pure membrane. Low selectivity of Matrimid/NH2-MIL-53 was due to the nonselective void formation at the interface between polyimide and MOF particle. For Ultem/MOF permeability of CO2 and CH4 and CO2/CH4 selectivity were higher than the neat Ultem since Ultem had better compatibility with MOF crystals.21

In another study, the Al based functionalized MOFs were embedded in Matrimid for CO2 and CH4 separations. A separation factor of about 36 was obtained for 15 wt % NH2-MIL-101(Al). For 20 wt % NH2-MIL-53(Al) in Matrimid, although the CO2/CH4 separation factor increased 15%, CO2 permeability was decreased slightly compared with the pure membrane.22

The impact of NH2-MIL-53(Al) and NH2-MIL-101(Al) in sulfur-containing copolymides matrix (4,4’-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)–3,3’,4,4’-diphenylsulfonetetracarboxylic dianhydride (DSDA)/4-methylphenyl-2,4-pentan-1-one (4MPD)–4,4’-diaminodiphenyl sulfide (4,4’-SDA), 1:1 (polymer P1) and 6FDA/4MPD–4,4’-SDA 1:1 (polymer P2)) was studied by Seoane et al. for gas separation process. The permeation of H2O, CO2, and CH4 gases were tested through the membranes. The gas separation results for fillers with P1 were better than with P2 since the flexible SO2 groups in P1 had positive effect on the filler–polymer matrix interaction. NH2-MIL-101(Al), 10 wt % in P1, showed high permeabilities of 114, 71, and 1.7 barrer for H2O, CO2, and CH4, respectively.23

The performance of NH2-MIL-53(Al)/Matrimid@5218 MMM was reported by Rodenas et al. For 8 wt % loading of MOF, CO2 permeability was lower than the pure polymer. With further MOF loading up to 25 wt %, a 50% increment in CO2 permeability was observed with respect to the unfilled membrane. CO2/CH4 separation factor increased at 8 wt % loading while remaining unchanged at 25 wt % loading.24

Different types of fillers (ZIF-8, NH2-MIL-53, MCM-14, ETS-10, and silica) were used to fabricate MMMs with polysulfone (PSF) matrix by the spin coating method. Over 60% enhancement in H2/CH4 and O2/N2 separations was observed for an MMM containing NH2-MIL-53 compared with the pure polymer. Good affinity of NH2-MIL-53 toward PSF chains was responsible for better gas separation behavior of NH2-MIL-53 among the other fillers.25

Outstanding properties such as excellent mechanical strength, thermal stability, chemical resistance, and high capability of film forming have made poly(vinylidene fluoride) (PVDF) interesting for membrane industrial applications such as membrane distillation26 and membrane contactor.27 Generally PVDF has been recognized as a gas barrier material, and its application in gas separation membranes is of less importance. However, incorporating appropriate fillers into the PVDF matrix accompanied by PVDF modification can provide an opportunity to use this polymer for gas separation applications. Although PVDF is a semicrystalline polymer, it has flexible chains, which are expected to form an intimate interaction with fillers like MOFs. MIL-53(Al) materials were chosen to fabricate MMMs with PVDF. MIL-53(Al) is built up from AlO4(OH)2 octahedra infinite chains cross-linked by means of benzene dicarboxylate organic ligands. The three-dimensional microporous framework of MIL-53(Al) contains unidirectional diamond shaped channels with an internal diameter of 0.85 nm.28 NH2-MIL-53(Al) has an analogous structure based on MIL-53(Al) topology.29 Because of the flexible bond between Al3+ metal centers and organic ligands, both MIL-53(Al) and NH2-MIL-53(Al) exhibit special breathing behavior. However, their breathing behavior is different. Molecules that possess dipole or quadrupole moments such as CO2 and H2O can induce the breathing effect. In the absence of guest molecules, the large pore configuration is energetically dominant by 3 kJ/mol, the while strong interaction of guest molecules in low pressure with the hydroxyl group of MIL-53(Al) contracts pore size into the narrow pore configuration. The opposite breathing behavior is reported for the amino-functionalized MIL-53(Al). Unlike MIL-53(Al), for NH2-MIL-53(Al) the narrow pore configuration is more stable than large pore by 14 kJ/mol in the absence and at low pressure of CO2. It expands to its large pore configuration at high pressure of CO2.30 In addition, high surface area, large pores, and chemical resistance of the MIL-53 series are also responsible for their excellent tendency for the selective adsorption of CO2. In the case of NH2-MIL-53(Al), the presence of amino functional groups increases both CO2 adsorption and interaction with existing functional groups in the polymer matrix, which result in high CO2/CH4 separation.18

In the present study, poly(vinylidene fluoride) (PVDF) was chemically modified by using KMnO4 and KOH as oxidant and strong base. The chemical modification led to creation of some functional groups in the polymer chains. Then the modified PVDF (M-PVDF) was used to fabricate MMMs with MIL-53(Al) and NH2-MIL-53(Al). The impact of chemical modification and MOF loadings on CO2/CH4 separation properties of PVDF was evaluated by measuring the gas permeability and selectivity.

2. EXPERIMENTAL SECTION

2.1. Materials. N,N-Dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), acetone, Al(NO3)3·9H2O, 1,4-benzenedicarboxylic acid and 2-amino-1,4-benzenedicarboxylic acid (NH2-H2BDC), KOH, and KMnO4 were received from Sigma-Aldrich.

2.2. Modification of PVDF. PVDF was modified according to a procedure that was published previously.31 PVDF powder was poured into an aqueous solution of KOH (0.5 mol/L) and KMnO4 (1.0%). The reaction was kept at 60 °C for 10 min. The color of PVDF changed from white to brown. The brown precipitate was filtered and moved to an acidic solution of 1.2% NaHSO3 until it regained the white color. Finally the modified PVDF was washed 2 or 3 times with distilled water and dried at room temperature under vacuum for 48 h.
2.3. MOF Preparation. The MIL-53(Al) and NH$_2$-MIL-53(Al) MOFs were synthesized according to the method described in a previous study. In the synthesis of MIL-53(Al), measured amounts of Al(NO$_3$)$_3$·9H$_2$O (0.375 g) and 1,4-benzenedicarboxylic acid (0.268 g) were added to DMF (14 mL) under stirring. The solution was moved to a Teflon lined steel autoclave in an oven at 130 °C for 3 days. The obtained white crystals were washed with DMF to remove unreacted reagents. A Soxhlet extractor was utilized to replace DMF with a solvent with a low boiling point like acetone. The resulting white crystals were washed with DMF to remove unreacted reagents. A Soxhlet extractor was utilized to replace DMF with a solvent with a low boiling point like acetone. The resulting crystals were dried at 100 °C for 24 h. The same procedure was used to synthesize NH$_2$-MIL-53(Al) replacing 1,4-benzenedicarboxylic acid with 2-aminoterephthalic acid.

2.4. Preparation of M-PVDF Dense Membrane. The dense film casting method was applied to fabricate membranes. The polymer powder was kept under vacuum at 100 °C for 24 h to remove any adsorbed moisture. Then the solution of 10% polymer in DMAc was prepared at room temperature during 48 h. Thereafter, the solution was degassed to draw out any bubble created during stirring. After complete degassing, the solution was cast onto a glass substrate and dried at 80 °C in an oven for 12 h. Finally, the membrane was kept in a vacuum oven for 24 h at 120 °C in order to remove any remnant solvent.

2.5. Preparation of Mixed Matrix Membranes. All of the mixed matrix membranes were prepared as follows. The measured amount of MOF was added to DMAc solvent, and the mixture was stirred for 24 h. In addition, bath sonication was used for 20 min to make sure that the MOF was homogeneously dispersed in the solvent. The polymer was added to the MOF solution using the priming technique. The priming technique can enhance adhesion between the polymer and MOF, thus improving the gas separation properties of membranes. In this regard, 10% of polymer was added to the mixture, and the solution was mixed for 5 h. Thereafter the remaining amount of polymer was added, and stirring was continued to obtain a uniform mixture. After the solution was degassed, it was cast onto a glass substrate and dried with the same treatment that was used for the dense membrane. Mixed matrix membranes comprising 5% or 10% MIL-53(Al) and NH$_2$-MIL-53(Al) in M-PVDF were fabricated to compare their gas separation efficiency. The required amounts of MOFs were calculated based on the following equation:

\[
\text{MOF loading} = \left( \frac{\text{wt MOF}}{\text{wt MOF} + \text{wt polymer}} \right) \times 100
\]

2.6. Gas Permeation Measurement. Permeability determination of pure gases was implemented by using the variable pressure/constant volume method for all of the membranes. This method is appropriate for membranes with low permeability. The whole system was evacuated for 4 h before every measurement. The pressure of the penetrating gas in the upstream chamber was fixed at the desired amount. A high precise pressure transducer (0–100 mbar, BD sensors, Germany) was used to monitor pressure change in downstream chamber. Permeability and ideal selectivity were calculated using the following equations:

\[
\begin{align*}
P& \text{(barrer)} = \frac{273.15 \times 10^{10}Vt}{760 \times 76ATP} \left( \frac{dP}{dt} \right) \\
\text{selectivity} &= \frac{P}{P_i}
\end{align*}
\]

where \(t\) is membrane thickness (cm), \(V\) is the volume of the downstream chamber (cm$^3$), \(A\) is the membrane surface area (cm$^2$), \(T\) is the experimental temperature (K), \(P\) is feed pressure, and \(\frac{dP}{dt}\) is the pressure gradient (mmHg/s) in the downstream chamber. In this study, \(i\) and \(j\) are CO$_2$ and CH$_4$ permeabilities, respectively. The following equation was used to calculate the separation factor (\(\alpha_{ij}\)) of membranes in a binary gas mixture of CO$_2$ and CH$_4$ with ratio of 1:1.

\[
\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j}
\]

where \(x\) and \(y\) are mole fractions of gases in feed and permeate, respectively. The composition of feed and permeate in mixed gas test was determined by GC analysis. After reaching the steady state, at least four measurements were done at different times, and the average values were reported.

2.7. MOF and Membrane Characterization. Field emission scanning electron microscopy (FESEM; HITACHI, model S4160) was used to study morphology of the MOFs and particle–polymer interface. The membranes were broken in liquid nitrogen and covered with a thin layer of Au. A differential scanning calorimeter (Netzsch DSC 200F3) has been used to determine the melting temperature of selected membranes. The membranes were kept at 40 °C, and then the temperature was increased to 200 °C with a heating rate of 5 °C/min under a nitrogen atmosphere. The melting temperatures (\(T_m\)) and fusion heat (\(\Delta H\)) of the selected membranes were reported. Powder X-ray diffraction patterns of the prepared membranes were achieved by using an X-ray diffraction instrument (Siemens D5000) with a Cu target (\(\lambda = 0.1540 \text{ nm}\) at RT over a 2\(\theta\) range from 0 to 50°). Thermal resistance of the prepared membranes was investigated with a PL thermogravimetric analyzer (TGA 1000, UK). The TGA curves were obtained over the temperature range of 30 to 800 °C with a heating rate of 10 °C/min under a nitrogen stream. Physisorption of nitrogen for MOFs was done with a Belsorp mini II, BelJapan, instrument at 77 K. Surface area of the samples was calculated by the Brunauer–Emmet–Teller (BET) method. Mechanical properties of the membranes were evaluated by a Z030 Zwic/Roell testing machine at room temperature with an operating rate of 1 mm/min. FT-IR spectra of MOFs were recorded with Bruker FT-IR spectrometer.
MOFs are depicted in Figure 1. From the comparison of PVDF FT-IR before and after modification, the absorption peaks appearing at 1703 and 3200−3600 cm$^{-1}$ indicated that modification of PVDF was accomplished successfully. The former was related to the carbonyl group, and the latter showed hydroxyl group existence in M-PVDF. In the first step of modification, HF was eliminated, and during the nucleophilic addition reaction, the OH groups were created in PVDF chains. The existence of C=O groups might be due to the oxidation of modified polymer in the air.31 It should be noted that the peak at 2900 cm$^{-1}$ was attributed to the CH$_2$ group. In the case of pure MOFs, characteristic peaks at 1511 and 1597 cm$^{-1}$ were assigned to the asymmetric stretching vibration of COO, and the absorption peak at 1416 cm$^{-1}$ was attributed to the symmetric stretching vibration of COO. The absorption peaks at 3380 and 3490 cm$^{-1}$ in functionalized MOF were attributed to NH$_2$ asymmetric and symmetric stretching vibrations. Formation of hydrogen bonds between the M-PVDF and MOFs could be the reason for good interaction of both phases. The observed shift in characteristic peaks related to the MOFs or polymer confirmed hydrogen bond formation, which has been reported by other researchers.32,33 The peak related to the carbonyl of M-PVDF was shifted to 1762 and 1790 cm$^{-1}$ for 10% loaded M-PVDF with MIL-53(Al) and NH$_2$-MIL-53(Al), respectively. The three peaks attributed to the C=O of MOFs were transferred to other wavenumbers for the prepared MMMs. NH$_2$ absorption bands were located at lower frequency for the MMM compared with the pure NH$_2$-MIL-53(Al). NH$_2$ absorption bands appeared at 3373 and 3488 cm$^{-1}$ for the MMM containing 10% functionalized MOF.

The membrane’s surface property was determined by contact angle test. Table 2 shows the effect of modification and MOF loading on variation of water contact angle of PVDF. The pure PVDF membrane showed a contact angle of 89°. After modification of PVDF, the contact angle decreased to 56° indicating the formation of hydrophilic groups in PVDF as was proven by FT-IR analysis. The hydrophilic nature of the membranes increased in the presence of MOF particles due to the hydrophilic nature of the fillers with surface OH groups. The contact angle of MMMs containing 10 wt % MIL-53(Al) and NH$_2$-MIL-53(Al) was decreased by 48.3% and 49.4% compared with pure PVDF membrane.

Figure 2. SEM images of prepared membranes: (a) pure M-PVDF, (b) M-PVDF/MIL-53(Al), and (c) M-PVDF/NH$_2$-MIL-53(Al) with two different magnifications.

### Table 1. Characteristics of the Synthesized MOFs

<table>
<thead>
<tr>
<th>MOF</th>
<th>Structure</th>
<th>Pore Channel</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Ref</th>
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<tr>
<td>MIL-53</td>
<td>3D</td>
<td>1D</td>
<td>1130.19</td>
<td>0.56</td>
<td>34</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1118</td>
<td>0.36</td>
<td>35</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1140</td>
<td>0.36</td>
<td>36</td>
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<td></td>
<td></td>
<td></td>
<td>1365</td>
<td>0.433</td>
<td>18</td>
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<td></td>
<td></td>
<td>1408</td>
<td>0.462</td>
<td>33</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1170</td>
<td>0.424</td>
<td>this work</td>
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<tr>
<td>NH$_2$-MIL-53</td>
<td>3D</td>
<td>1D</td>
<td>735</td>
<td>0.240</td>
<td>18</td>
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<tr>
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<td></td>
<td></td>
<td>795</td>
<td>0.258</td>
<td>33</td>
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<td>780</td>
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<td>37</td>
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<td></td>
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<td>782</td>
<td>0.246</td>
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</table>

### Table 2. Contact Angle of Prepared Membranes

<table>
<thead>
<tr>
<th>MOF Loading</th>
<th>MIL-53(Al)</th>
<th>NH$_2$-MIL-53(Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>66.7 ± 0.4</td>
<td>66.7 ± 0.4</td>
</tr>
<tr>
<td>5</td>
<td>56.5 ± 0.6</td>
<td>54.4 ± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>46.8 ± 0.3</td>
<td>45.3 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 1. FT-IR spectra of (a) MIL-53(Al), (b) NH$_2$-MIL-53(Al), (c) PVDF, (d) M-PVDF, (e) M-PVDF/MIL-53(Al)-10%, and (f) M-PVDF/NH$_2$-MIL-53(Al)-10%.

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The X-ray mapping of membrane cross sections accordingly showed good particle dispersion as well (Figure 3). No “sieve-in-a-cage” morphology was detected in SEM images, and matching of MOFs and polymer matrix were excellent. In addition, increase in plastic deformation of the polymer matrix in MMMs compared with the pure membrane could confirm the complementary contact between particles and M-PVDF. Plastic deformation of the polymer matrix was due to the interfacial stress during cryogenically fracturing membranes in liquid nitrogen. The interfacial stress was created because of the strong interaction between phases.38,39

To determine the crystal structure of membranes, XRD analysis was performed. Four common crystal phases (α, β, γ, δ) have been reported for PVDF. Crystallinity of PVDF is one of the most important factors influencing its mechanical properties. Meanwhile the nonpolar α phase has been known as the most common crystal phase of PVDF. With exposure of α phase to different conditions like mechanical stretching, electric field, high-temperature, etc., other crystal phases can be obtained. So crystal content of PVDF membranes based on experienced conditions is different. There have been studies to investigate the effects of variables on crystalline structure of PVDF membranes.40−43

The XRD patterns of pure membranes and M-PVDF/MOF MMMs are shown in Figure 4. The observed characteristic peaks at θ = 17.06°, 18.3°, and 20.17° for M-PVDF were similar to the original PVDF membrane. These peaks were assigned to (100), (020), and (110) lattice planes of the α phase, respectively. The β phase was absent in XRD patterns of pure membranes since the related peak did not emerge in the spectrum. This demonstrated that the dominant crystal phase in PVDF or the modified one was α phase. No considerable change in crystal phase of the polymer matrix was observed upon embedding of MOFs in M-PVDF. The pattern of MMMs exhibited the peaks related to the crystalline structure of MIL-53(Al) and NH2-MIL-53(Al). Lack of matching in the XRD pattern of NH2-MIL-53 based MMM with NH2-MIL-53 particle was due to the pore configuration of MOF particle. The flexible framework of the MOF was changed from narrow pore form after synthesis to its large pore configuration in the MMM. This configuration variation could be attributed to partial penetration of polymer chains in the pore structure of the NH2-MIL-53(Al). The same phenomenon was reported in previous work and other literature.24 So the ordered crystalline structure of the MOFs was maintained in the MMMs during membrane preparation.

Figure 3. X-ray mapping of the cross section of (a) PVDF/MIL-53(Al) and (b) PVDF/NH2-MIL-53(Al).

Figure 4. XRD patterns of (a) MIL-53(Al), (b) NH2-MIL-53(Al), (c) pure PVDF, (d) pure M-PVDF membrane, and MMMs containing 10 wt % of (e) MIL-53(Al) and (f) NH2-MIL-53(Al).

Figure 5 presents TGA curves of the prepared membrane. Thermal stability of pure M-PVDF membrane decreased slightly compared with the pure PVDF. This could be due to the introduction of hydroxyl group in PVDF through the modification process. Although PVDF possesses excellent chemical resistance, alkaline exposure of PVDF diminished its stability considerably. Despite the good interaction of MOFs and M-PVDF, thermal stability of their MMMs decreased substantially. Degradation temperature (Td) of pure M-PVDF and of M-PVDF 10% loaded with MIL-53(Al) and NH2-MIL-53(Al) were reported as 470, 386, and 386 °C, respectively. As was mentioned in previous work, lower thermal stability of MOFs relative to the polymer matrix, thermal degradation products of MOFs and M-PVDF, and interaction of HF with these degradation products could be responsible for such a considerable decrease in the decomposition temperature of MMMs. It is worth noting that Td of M-PVDF 10% loaded with MIL-53(Al) and NH2-MIL-53(Al) was slightly higher than that of MMMs with PVDF. Affinity of MOFs toward M-PVDF was
probably stronger than with PVDF due to the presence of carbonyl and hydroxyl groups in M-PVDF structure.

The DSC curves of pure PVDF, M-PVDF, and MMMs containing 10 wt % MIL-53(Al) and NH2-MIL-53(Al) are illustrated in Figure 6. Melting temperature ($T_m$), fusion heat ($\Delta H$), and crystallinity ($\chi$) of the selected membranes are given in Table 3. The following equation was applied to calculate the crystallinity of membranes:

$$\chi = \frac{\Delta H^o}{W \Delta H} \times 100\%$$

where $\Delta H^o$ is the fusion heat and $W$ is the polymer content in the MMMs. A value of 90.4 J/g was used for PVDF with 100% crystallinity of $\alpha$ phase.

Pure M-PVDF showed higher fusion heat and crystallinity. For pure M-PVDF, $T_m$, $\Delta H$, and $\chi$ were determined as 163.2°C, 29.85 J/g, and 36.68% respectively. Melting temperature of M-PVDF and its MMMs with MIL-53(Al) and NH2-MIL-53(Al) was around 163 °C similar to that of PVDF and PVDF/ MOFs. Incorporation of MOFs into the M-PVDF increased crystallinity of the matrix up to 49.01% and 50.9%. The MOFs might play the role of nucleation agent role during the crystallization of polymer due to the hydrogen bond formation between the two phases. In addition, the thermogram of M-PVDF/MOF MMMs showed two peaks. While the first small peak was related to the melting of a trans-crystalline layer between MOF particles and polymer matrix, the melting of the semicrystalline polymer matrix created the second peak. Similar results were reported by Xu et al.46 for PVDF/carbon nanotube (CNT) composites. Xu et al. reported DSC curves with two peaks for PVDF with different CNT contents. Moreover, crystallinity of M-PVDF/MOF MMMs was higher than that of the MMMs of PVDF and the same MOFs due to the strong M-PVDF/MOF interaction. This increment was more pronounced for nonfunctionalized MOF than the functionalized one. This could confirm that the modification of PVDF influenced the interfacial region considerably.

Tensile tests were used to investigate the impact of MOFs on the mechanical properties of the membranes. The Young’s modulus, tensile strength, and elongation at break of pure membranes and MMMs with 5 and 10 wt % MOF are listed in Table 4. Young’s modulus of MMMs was improved compared with that of the pure PVDF and M-PVDF. Increase in crystallinity of membranes by incorporating MOFs should be considered in Young’s modulus improvement. So, higher Young’s modulus of M-PVDF containing both MOFs relative to PVDF/MOFs confirmed the positive effects of the modification process on properties of membranes. Both tensile strength and elongation at break of MMMs decreased compared with those of the pure membranes. This downward trend indicated that flexibility of membranes has been reduced due to the presence of MOFs in the polymer matrix.

### 3.3 Gas Transport Properties of Membranes

#### 3.3.1 Gas Permeability, Ideal Selectivity and Separation
Table 5. Gas permeability, ideal selectivity and (50/50) CO2/CH4 mixed gas separation factor (α) of membranes measured at 298 K and a feed pressure of 5 bar

<table>
<thead>
<tr>
<th>sample</th>
<th>permeability (barrer)</th>
<th>ideal selectivity</th>
<th>separation factor (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO2</td>
<td>CH4</td>
<td>CO2/CH4</td>
</tr>
<tr>
<td>pure PVDF</td>
<td>0.915 ± 0.121</td>
<td>0.043 ± 0.011</td>
<td>21.27 ± 1.66</td>
</tr>
<tr>
<td>pure M-PVDF</td>
<td>1.201 ± 0.208</td>
<td>0.043 ± 0.009</td>
<td>27.93 ± 1.34</td>
</tr>
<tr>
<td>M-PVDF–MIL-53(Al) 5%</td>
<td>1.752 ± 0.169</td>
<td>0.049 ± 0.008</td>
<td>35.75 ± 1.76</td>
</tr>
<tr>
<td>M-PVDF–MIL-53(Al) 10%</td>
<td>2.454 ± 0.306</td>
<td>0.062 ± 0.008</td>
<td>39.58 ± 1.04</td>
</tr>
<tr>
<td>M-PVDF–NH2-MIL-53(Al) 5%</td>
<td>1.693 ± 0.224</td>
<td>0.045 ± 0.003</td>
<td>37.62 ± 1.55</td>
</tr>
<tr>
<td>M-PVDF–NH2-MIL-53(Al) 10%</td>
<td>2.240 ± 0.391</td>
<td>0.051 ± 0.010</td>
<td>43.92 ± 1.59</td>
</tr>
</tbody>
</table>

**Factor of Membranes.** Pure CO2 and CH4 measurements of prepared membranes, that is, permeability and ideal selectivity, were performed at 298 K and a feed pressure of 5 bar. At least two membranes were fabricated for each composition, and three permeation measurements were performed for each membrane. The average values were reported as the final results. For all membranes, CO2 permeation was considerably enhanced (Table 5).

For the pure modified PVDF, CO2 permeability increased, while CH4 permeability was the same compared with that of the pure PVDF membrane. So, about 31.3% and 26.3% increases in CO2/CH4 selectivity and separation factor were reported for the modified PVDF, respectively. This improvement could be due to the strong interaction between polar moieties in M-PVDF and CO2 gas with quadrupole moment. As shown in FT-IR (Figure 1), carbonyl and hydroxyl groups were created during the modification process of PVDF. In addition to M-PVDF backbone impact on CO2 transport, carbonyl and hydroxyl groups were in good contact with the MOF particles.

Incorporation 5 and 10 wt % MIL-53(Al) in M-PVDF increased permeability of pure gases, CO2/CH4 selectivity, and separation factor. With 5 wt % MIL-53(Al), 45.8% increment for CO2 permeability was observed relative to the pure M-PVDF. This increment increased to 104.3% for 10 wt % loading of MIL-53(Al). Significant increase in CO2 permeation could be attributed to the polymer matrix and MOF structure. CO2 gas has high affinity toward the hydroxyl groups of M-PVDF and MOF structure. Because of the special breathing effect of MIL-53(Al), pore configuration could be changed in the presence of guest molecules like CO2. In fact, adsorption of CO2 contracts the pores of MOF due to the interaction between CO2 and the hydroxyl group of MIL-53(Al). So, the configuration of MOF pores varies from large form to narrow form during CO2 adsorption.

Ideal CO2/CH4 selectivity increased 28% and 41.7% for 5 and 10 wt % MIL-53(Al) compared with that of the pure M-PVDF membrane. The same increment trend was observed for separation factor. This increase in CO2/CH4 selectivity and separation factor was even greater than that for the PVDF/MIL-53(Al) MMMs in previous work. The obtained results indicated that nonselective voids between MIL-53(Al) and PVDF disappeared when PVDF was modified. Lack of sufficient affinity of polymer toward the MOF leads to the nonselective void formation at the interfacial phase. Such voids deteriorate the performance of the MMMs. Chemical modification of PVDF increase its compatibility with the MOF. Good compatibility was the result of hydrogen bond formation between the two phases, polymer and MOF. In addition, unoccupied metal ions in MOFs could be coordinated to the carbonyl groups in M-PVDF. This good interaction was confirmed by FT-IR analysis. Moreover, lack of interaction between CH4 and membrane accompanying the reduction in pore size of MIL-53(Al) due to the breathing effect limited CH4 transport through membrane.

Embedment of NH2-MIL-53(Al) in M-PVDF improved the gas permeability, ideal selectivity and separation factor. In addition to polymer matrix polar groups, the NH2-MIL-53(Al) particles played an important role in superior CO2 permeation. Introduction 5 wt % NH2-MIL-53(Al) in M-PVDF showed 41% and 53% CO2 permeation improvement with respect to the pure M-PVDF and NH2-MIL-53(Al)/PVDF MMM with the same loading. With further loading to 10 wt %, the CO2 permeation increment increased up to 86.5% and 59.3%, respectively. Reversible reaction of NH2 groups in the MOF structure with CO2 result in carbamate formation, which favored CO2 adsorption and permeation.

CO2/CH4 ideal selectivity and separation factor of NH2-MIL-53(Al)/M-PVDF MMMs substantially increased with respect to not only the pure M-PVDF but also the NH2-MIL-53(Al)/PVDF MMMs. Besides the good compatibility between the particles and M-PVDF, some polymer chain rigidification might occur around particles. Chain rigidification was the result of movement inhibition of M-PVDF in the polymer–MOF interfacial area. This occurrence distinguished the penetrating gases with different molecule size. Thus, for NH2-MIL-53(Al)/M-PVDF, the CO2 permeation was enhanced while CH4 permeation decreased compared with the NH2-MIL-53(Al)/PVDF and consequently CO2/CH4 ideal selectivity and separation factor significantly increased.

Comparing NH2-MIL-53/M-PVDF with MIL-53/M-PVDF, the gas permeability dropped and selectivity increased. Lower gas permeability of MMMs containing NH2-MIL-53(Al) compared with that of with the nonfunctionalized MOF was attributed to the larger pore size of MIL-53(Al) than NH2-MIL-53(Al). Since pore size of the MIL-53(Al) (7–8 Å) is much larger than the kinetic diameters of CO2 (3.3 Å) and CH4 (3.8 Å), both CO2 and CH4 gases can pass through the MOF pores.55 In contrast, the smaller pore size of NH2-MIL-53(Al) led to less gas transport. Higher CO2/CH4 ideal selectivity and separation factor of NH2-MIL-53(Al) could be relevant to the better compatibility with M-PVDF and strong affinity of NH2 toward CO2.

The obtained results and related results from the literature are depicted in Figure 7. As it can be seen, the performance of M-PVDF based mixed matrix membranes improved significantly compared with that of unmodified PVDF. Furthermore, with modification of PVDF, the results can be comparable to other results from literature.2,39,40,50

### 3.3.2. Effect of Feed Pressure

The effect of feed pressure on gas performance was explored for pure M-PVDF, M-PVDF/NH2-MIL-53(Al) 10% and M-PVDF/NH2-MIL-53(Al) 10%. The...
difference between performance of the pure membrane and MMMs at elevated pressure is depicted in Figure 8. With increasing pressure, CO₂ permeability and separation factor of the pure membrane decreased, as reported in the literature.¹⁸,⁵¹ For MMMs, CO₂ permeability dropped and separation factor increased with increasing pressure. The same trends were reported using NH₂-MIL-53(Al) and MIL-53(Al) MOFs in a polymer matrix in the literature.¹⁸,¹⁹,⁵² The observed gas transport of M-PVDF/NH₂-MIL-53(Al) 10% at higher pressure could be explained by MOF gas transport property. Although, increase in feed pressure increases CO₂ adsorption capacity of the MOF, it does not increase CO₂ diffusivity through the MOF. Thus, increase in separation factor suggests that strong interaction of CO₂ with MOF at higher pressure excludes CH₄ molecules from the MOF. Reduction in CH₄ accompanied by the selective CO₂ adsorption by the MOF leads to increase in separation factor of MMMs.

### 3.3.3. Comparing the Experimental Data of MMMs with the Prediction Models

Most theoretical models for prediction of gas transport of MMMs are adapted from thermal/electrical conductivity models due to the resemblance between gas permeability through MMMs and thermal/electrical conductivity in composites. Different permeation models have been used to predict gas separation behavior of MMMs with both interfacial ideal and nonideal morphologies. Maxwell,⁵³ Bruggeman,⁴⁴ Lewis–Nielsen,⁵⁵ and Pal⁵⁶ are the common models to describe the ability of a MMM (Pₑₑ) with an ideal morphology to separate gases. The effective steady-state permeability of gaseous species through an MMM based on the Maxwell model can be calculated using the following equation:

\[
Pₑₑ = P_c \left( \frac{1}{\phi_d} \right) \left( \frac{\alpha}{\alpha + 1} \right) = \left( \frac{P_r}{\phi_d} \right)
\]

where \(\phi_d\) is the volume fraction of the dispersed phase and \(\alpha\) is the permeability ratio, \(P_d/P_c\) (\(P_c\) and \(P_d\) are continuous and dispersed phase permeabilities, respectively).

While the Maxwell model is applicable for low loadings (\(\phi_d < 0.2\)), the Bruggeman model predicts permeability of gaseous species for a larger range of \(\phi_d\). However, both models suffer from the same limitations in which particle size distribution, particle shape, and particle aggregation are ignored in these two models.

\[
(P_r)^{1/3} \left( \frac{\alpha - 1}{\alpha} \right) = (1 - \phi_d)^{-1}
\]

where \(P_r = Pₑₑ/P_c\).

In the Lewis–Nielsen model, the effect of particle morphology on permeability behavior of MMMs is considered by using the parameter \(\phi_m\) (the maximum packing volume...
fraction of filler particles). The Lewis–Nielsen is reduced to the Maxwell model when $\phi_m \rightarrow 1$.

$$P_{\text{eff}} = P \left[ 1 + \frac{2\phi_n(a - 1)}{(\alpha + 2)} \right]$$

where

$$\psi = 1 + \left(1 - \frac{1 - \phi_m^2}{\phi_m^2} \right)$$

The Pal model reduces to the Bruggeman model at $\phi_m \rightarrow 1$.

$$P_{\text{eff}} = \left( \frac{\alpha - 1}{\alpha - P} \right)^{1/3} \psi$$

Comparing experimental data with the calculated result obtained from prediction models is a useful tool for considering the interfacial phase morphology of polymer and filler particles in a MMM as an ideal or nonideal morphology. In this regard, CO$_2$ permeation of the prepared MMMs was calculated with the four above-mentioned models, Maxwell, Bruggeman, Nielsen–Lewis, and Pal. The obtained results are shown in Figure 9 and listed in Table 6. The average absolute relative errors (%AARE) were calculated to estimate the gas permeability values of pure MOFs. The minimum difference between experimental and prediction results gives the best values of CO$_2$ permeabilities of the pure MOFs.

$$\%AARE = \frac{100 \sum_{i=1}^{\text{NDP}} \left| \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right|}{\text{NDP}}$$

where NDP is the number of data points.

Less than 1% of AARE values for both MOFs (Table 7) shows that there is a good agreement between the experimental data and results of predictive models. SEM and FT-IR results confirmed the good matching between both MOFs and polymer. Polymer matrix polar groups form hydrogen bonds.

### Table 6. Gas Permeabilities and Ideal Selectivities of MMMs Containing MOFs Predicted by the Maxwell, Bruggeman, Lewis–Nielsen, and Pal models

<table>
<thead>
<tr>
<th>MOF</th>
<th>gas permeability and selectivity</th>
<th>MOF wt %</th>
<th>experiment</th>
<th>Maxwell</th>
<th>Bruggeman</th>
<th>Lewis–Nielsen</th>
<th>Pal</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-53</td>
<td>$P_{\text{CO}_2}$</td>
<td>18</td>
<td>1.752</td>
<td>1.781</td>
<td>1.786</td>
<td>1.765</td>
<td>1.754</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32</td>
<td>2.454</td>
<td>2.452</td>
<td>2.453</td>
<td>2.450</td>
<td>2.456</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>11.3</td>
<td>10.2</td>
<td>10.2</td>
<td>9.8</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>$P_{\text{CO}<em>2}/P</em>{\text{CH}_4}$</td>
<td>18</td>
<td>35.75</td>
<td>36.35</td>
<td>36.45</td>
<td>36.02</td>
<td>35.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32</td>
<td>39.58</td>
<td>39.55</td>
<td>39.56</td>
<td>39.52</td>
<td>39.61</td>
</tr>
<tr>
<td>NH$_2$-MIL-53</td>
<td>$P_{\text{CO}_2}$</td>
<td>18</td>
<td>1.693</td>
<td>1.720</td>
<td>1.703</td>
<td>1.684</td>
<td>1.674</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32</td>
<td>2.240</td>
<td>2.241</td>
<td>2.239</td>
<td>2.242</td>
<td>2.238</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>9.6</td>
<td>7.5</td>
<td>7.0</td>
<td>7.0</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>$P_{\text{CO}<em>2}/P</em>{\text{CH}_4}$</td>
<td>18</td>
<td>37.62</td>
<td>38.22</td>
<td>37.84</td>
<td>39.22</td>
<td>37.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32</td>
<td>43.92</td>
<td>43.94</td>
<td>43.90</td>
<td>43.96</td>
<td>43.88</td>
</tr>
</tbody>
</table>

### Table 7. %AARE of Prediction Models

<table>
<thead>
<tr>
<th>prediction models</th>
<th>CO$_2$ gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIL-53(Al)</td>
</tr>
<tr>
<td>Maxwell</td>
<td>0.87</td>
</tr>
<tr>
<td>Bruggeman</td>
<td>0.99</td>
</tr>
<tr>
<td>Lewis–Nielsen</td>
<td>0.45</td>
</tr>
<tr>
<td>Pal</td>
<td>0.10</td>
</tr>
</tbody>
</table>
with the OH or NH₂ groups of the MOFs. This bond formation prevents the creation of nonselective voids in the interfacial phase. In addition to interfacial interaction, fair distribution of MOF particles in the M-PVDF matrix can be concluded from the experimental and theoretical result matching, too.

4. CONCLUSION

Poly(vinylidene fluoride) was chemically modified by using KOH and KMnO₄. According to the FT-IR analysis and contact angle measurements, carbonyl and hydroxyl groups were created in the PVDF structure during the modification. Increase in hydrophilicity of PVDF led to decrease in contact angle. Thus, lower contact angle of M-PVDF relative to the original PVDF indicated that modification of PVDF was successful. In addition, incorporation of MOFs in M-PVDF caused the decrease in contact angle of MMMs due to the existence surface hydrophilic groups in MOFs. Crystallinity of M-PVDF was enhanced with incorporation of MIL-53(Al) and NH₂-MIL-53(Al) while melting temperature did not vary significantly. Thermal stability of M-PVDF/MOF MMMs decreased significantly relative to the M-PVDF. However, this stability was slightly more than the PVDF/MOF MMMs. The same α crystal phase of PVDF was shown in the XRD pattern for M-PVDF and incorporation of MOFs in M-PVDF did not change the α crystal phase in polymer matrix. Thermograms of MMMs showed two peaks: the small one was related to melting of the transcristalline layer between particles and polymer and the sharp peak was due to the melting of the semicrystalline polymer. The SEM images revealed no detectable voids between MOF and matrix, and the particles were dispersed in the polymer uniformly. Increase in Young’s modulus of MMMs compared with pure membrane showed the positive effects of the modification process on the mechanical properties of membranes. The shift in some characteristic peaks in FT-IR spectra of MMMs was observed compared with the pure MOFs and M-PVDF. This confirmed that the MOFs were in a good interaction with M-PVDF matrix. Clearly, both CO₂ permeability and CO₂/CH₄ selectivity were increased by modification on PVDF. This enhancement improved with incorporation of the MOFs with excellent affinity toward CO₂. Increase in CO₂ permeation was due to the interaction of CO₂ with MOFs and polymer matrix. High observed CO₂/CH₄ selectivity confirmed excellent matching of MOFs and M-PVDF. Thus, the chemical modification process not only improves gas separation performance of PVDF significantly but also did not deteriorate its chemical and mechanical properties.

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Notes

The authors declare no competing financial interest.

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