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Tailoring the CO$_2$ permeation of Pebax1657/polyether imide thin film composite membrane via embedding Ag-based metal-organic framework

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Abstract

Thin-film composite/nanocomposite (TFC/TFN) membranes count as the latest version of carbon capture membranes characterized by their excellent gas permeance, great selectivity, cost-effectiveness, and the ability to separately manage and tune the constituents of the individual layer. In this regard, Pebax®1657 embedded with synthesized Ag-BTC metal-organic frameworks (MOFs) was coated on the polyether imide (PEI) support layer to produce TFNs. To assess the impacts of Ag-BTC particles (carboxyl-rich surface particles) on the features of the constructed TFC/TFN membranes and their gas permeation qualities, several CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation experiments (mixed and pure gas testing) were carried out. Ag-BTC particles were distributed appropriately within the Pebax1657 matrix, improving the gas permeability (particularly for CO$_2$) and enhancing CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation factors. A simultaneous increase in CO$_2$ permeability and gas pair selectivities was observed with rising feed pressure. A 394.97 Barrer CO$_2$ permeability and 38.20 CO$_2$/N$_2$ and 21.25 CO$_2$/CH$_4$ selectivities were obtained for the TFN filled with 3 wt.% Ag-BTC at 10 bar and 30 °C. A mixed gas test also showed a similar trend but lower values than a pure one. The results for the humidified conditions exhibited higher CO$_2$ permselectivities in comparison with the dry gas given the water molecules facilitate the CO$_2$ transportation through the Pebax®1657 matrix. Finally, enhancing Ag-BTC filler content and increasing the input pressure provided excellent conditions for approaching Robeson’s limit.

Keywords:
CO$_2$ separation, Ag-BTC particles, Pebax®1657, thin film composite membrane, permeability
1. Introduction

Gas separation using membrane technology has developed into a significant industrial process during the past 30 years. Membrane technology has shown a high potential for replacing current techniques of CO₂ separation from various streams (i.e., amine solutions, adsorption procedure, cryogenics) owing to high energy efficiency, low investment, ease of operation, small footprint, easy scale-up, compactness and modularity, and environmental friendliness, to mention a few [1-8]. Several applications, including oxyfuel combustion systems (O₂ from N₂), purge gas recovery (NH₃, H₂, N₂, Argon), upgrading landfill gas to biomethane, natural gas dehydrating, acid gas removal (H₂S, SO₂, COS), and pre/post-combustion system (CO₂ removal), have made extensive use of membrane technology [9-11].

From the industrial point of view, an ideal membrane should have a) high permeability, b) reasonable selectivity, c) fair price, and d) facile film formation. Nonetheless, the available polymers (organic or inorganic compounds) hardly fulfill such requirements. In recent years, mixed matrix membranes (MMMs)– created via uniformly scattering inorganic and organic nanoparticles within hosting polymer matrices– have been the most extensively studied membranes because of their CO₂ separation performance, feasibility to greatly exceed the inherent limitations of single polymeric membranes (i.e., the trade-off effect, low stability, short lifetime) as well as being highly processable and cheaper in comparison with ceramic membranes [12-14].

The most crucial element in the fabrication of MMMs is making the dense layer crack-free and as thin as possible. In general, the thickness of MMMs varies from ~20-200 µm. This huge physical thickness, in turn, would gravely affect the separation performance (lowering CO₂ permeability); thus, engineering the thickness of the membrane film seems imperative [15, 16]. In regards to this concern, an ultrathin film layer (≤ 1 µm) can substantially reduce mass transfer resistance which finally renders high CO₂ permeability and selectivity [12]. It must be also pointed out that nanoparticles can take up to a maximum of 50 % of the total weight of the membrane film. In a porous MMM, most of the embedded nanoparticles are placed in the porous layer beneath, hence the separation process is controlled by the dense skin of the membrane [13]. It means that the enormous potential of fillers is not yet fully exploited to improve removal efficiency. The constraints of MMMs have been circumvented by the development of TFC/TFN membranes with more complicated structural designs [13, 17, 18].
Multi-layered composite membranes involve a substrate bottom layer providing mechanical strength and an upper selective film defining separation functionality [12]. Other layers such as a protective layer, an intermediate (gutter) layer, and a highly porous non-woven underlayer can also be used to design high-performance gas separation membranes if needed [12]. An unrivaled feature of composite membranes is the independent optimization of each layer [19]. More importantly, the thin layers can be formed from almost any conceivable chemical combination [19]. Jeong et al. [19] were the first group who applied the TFC/TFN membranes for a separation process. They employed the interfacial polymerization technique to prepare 50-200 nm thick polyamide-NaA zeolite TFN membranes. Since then, several studies have been conducted on the effectiveness of thin film membranes for carbon capture [20-23].

The upper skin film is the main part of a composite membrane as it determines the overall separation performance [24]. Therefore, constructing prospective TFC/TFN membranes for effective CO₂ capture depends greatly on selecting the right materials. Among membrane materials, polymers (rubbery or glassy types), due to flexibility resulting from free rotation of segments around main chains, low manufacturing cost, availability, ease of processing, and surface modification have been at the center of attention [5, 25, 26]. Many different polymers are often used to create skin layers including polyvinylamine (PVAm) [18, 27], polyimides (PIs) [28, 29], polyactive [30-32], poly(1-trimethylsilyl-1-propyne) (PTMSP) [33-35], poly(dimethylsiloxane) (PDMS) [36-39], polymers of intrinsic porosity (PIMs) [40-42], polyethylene glycol (PEG) [43-46], and the most used Pebax [15, 16, 47-57]. Industrially, a membrane system with a high processing capacity and an adequately high permselectivity for CO₂/gas is required to compete with other traditional separation techniques [58]. To obtain high CO₂ selectivity, the selected polymer must also have high reactivity selectivity or solubility selectivity. For reactivity selectivity, it relates to facilitated transport membranes. In membrane separation processes, facilitated transport (FT) refers to a coupled transport mechanism composed of two primary effects: pure physical diffusion and reversible chemical reaction between the target solute (A) and the carrier (C). At the feed side of the membrane, the solute reacts and the reaction product (AC), also known as “complex” in the usual terminology of FT, diffuses across the thickness. The reversed chemical reaction releases the solute at the downstream end [59]. On the other hand, for the solubility selectivity mechanism, interactions between the desired gas and the chains of polymer define mass transport. In this regard, a favorable polymer must contain abundant functional moieties with a special tendency for CO₂ gas [60]. A facile way is the introduction of
CO\textsubscript{2}-philic moieties like ethylene oxide (EO) units in the polymer lattice that strongly interact with CO\textsubscript{2} molecules through dipole-quadrupole interactions [61, 62]. Pebax membranes – a class of thermoplastic elastomers multiblock copolymers sold under the trademark Pebax and composed of rigid polyamide (PA) segments and flexible polyether (PE) segments covalently bounded– have been extensively evaluated for different separation purposes because of their elevated CO\textsubscript{2} permeability, high CO\textsubscript{2} separation factor coupled with enhanced mechanical strength [12, 58, 62]. The great CO\textsubscript{2} selectivity is attributed mostly to the potent interaction between polyethylene oxide (PEO), which contains polar ether oxygen atoms, and CO\textsubscript{2}.

Recently, Martinez et al. [47] incorporated [Bmim][BF\textsubscript{4}] ionic liquid (IL), ZIF-94, and ZIF-8 nanoparticles into the Pebax Renew 30R51 matrix (a 41% renewable carbon content). The final selective layer was then spin-coated onto the PTMSP/PSf supports. The 10 wt.% IL loading indicated the optimum function; in which a 27% (to 629 GPU) and 7% (to 29) rise in CO\textsubscript{2} permeance and CO\textsubscript{2}/N\textsubscript{2} separation factor were achieved because of the increased CO\textsubscript{2} mass transfer. Upon the insertion of 15 wt.% ZIF-94 and ZIF-8, respectively, the CO\textsubscript{2} permeance could rapidly escalate to 819 GPU (+65%) and 751 GPU (+51%) following the addition of ZIF particles, while almost maintaining a separation factor of 25 in both cases. The results authenticated the improved adaptability among the 30R51 lattice and ZIF nanoparticles in the presence of the IL.

Ranjbar et al. [63] first synthesized a PSf sublayer via the phase inversion technique and then immersed it in the Pebax1657/POP-CH\textsubscript{3} solution. The permeability of CO\textsubscript{2} and its relative selectivities were increased as POP particles were introduced into the TFC membrane. Compared to other gases, the smallest kinetic size, the greater condensability, and the robust interaction of quadrupole CO\textsubscript{2} and PA block facilitated the CO\textsubscript{2} permeation. Moreover, the benzene ring of POP-CH\textsubscript{3} and CO\textsubscript{2} could interact nucleophilically and electrophilically to increase the penetration of CO\textsubscript{2} across the prepared TFNs. At 2 bar and 5 wt.% of POP-CH\textsubscript{3} loading, the permeabilities of N\textsubscript{2}, CH\textsubscript{4}, and CO\textsubscript{2} gases moved from 3.30, 21.30, 218.10 Barrer to 4.50, 27.60, and 310.60 Barrer, respectively. Consequently, the CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} ideal selectivities grew from 65.54 to 70.04 and 10.01 to 11.25, respectively. The membrane’s performance was significantly improved as the input pressure reached 10 bar. The Pebax/POP-CH\textsubscript{3} 5 wt.% TFN membrane illustrated a high CO\textsubscript{2} permeability of 348.4 Barrer and its CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities were ~95 and ~14, respectively, at 10 bar.
Salestan et al. [52] grafted tetraethylenepentamine (TEPA) functionality on MIL-101 via a post-synthetic modification approach to figure out the effects of amino moieties on permselectivity properties. Next, the Pebax1657 filled with MIL-101-TEPA was dip-coated onto the polyether sulfone (PES) substrate. The CO$_2$ permeation rate and the selectivity of CO$_2$/CH$_4$ increased from 21.80 Barrer to 34.60 Barrer and from 21.10 to 46.3 after adding 5 wt.% of MOF particles, which means improvements of 63% and 110%, respectively. To justify the enhancement in separation efficiency, the following reasons were cited: (a) the improved compatibility between the polymer lattice and MOF particles after the amine-grafting procedure, which hindered the emergence of the interfacial spaces, (b) the enhanced molecular sieving capability of TFN membranes as a consequence of the reduced pore size and the enhanced micropore volume of amine-modified particles, and (c) the increase of mutual interactions of Pebax1657 chains and CO$_2$ in the presence of amine functional groups, which led to higher CO$_2$ solubility and thereby higher CO$_2$ permeability.

Mozafari et al. [64] evaluated the effects of novel CNF.UiO-66-NH$_2$ composite particles on the separation efficiency of the Pebax1657/poly(4-methyl-1-pentene) (PMP) composite membranes. The obtained results indicated a sharp upward trend in CO$_2$ permeability and CO$_2$/CH$_4$ selectivity. At ambient temperature and 6 bar, the Pebax1657/CNF.UiO-66-NH$_2$ (3 wt.%) membrane recorded a $\sim$328 Barrer CO$_2$ permeability and $\sim$27 CO$_2$/CH$_4$ factor. The corresponding values for mixed gas measurement were also 230 Barrer and 21, respectively. The reduction of crystal size by decorating the outer surface of CNFs with UiO-66-NH$_2$ led to better interfacial adaptability, which considerably reduced the creation of non-selective gaps. The enhanced interaction between the Pebax chains and fillers in the presence of NH$_2$ moiety of functionalized MOF also reduced the non-selective permeation, and hence the CO$_2$/CH$_4$ separation selectivity was increased. This demonstrated that the idea of decorating CNF with MOF counts as a highly productive way to enhance the separation efficiency of TFN membranes.

Maleh and Raisi [65] fabricated several TFNs composed of Pebax1657 polymer packed with zeolite NaX, SiO$_2$, and ZIF-8 particles coated on a PES substrate. The weight percentage of fillers ranged from 0-4 wt.% to determine the ideal composition (2 wt.%). The CO$_2$/N$_2$ separation factor substantially increased from 61.53 for the neat TFC membrane to 107.13 and 108.20 for the TFNs containing NaX and ZIF-8, respectively. Owing to its non-porous nature, the TFN containing 1 wt.% SiO$_2$ exhibited a CO$_2$/N$_2$ selectivity of about 82, considerably lower than those of other fillers. The permeability of CO$_2$ with ZIF-8 and SiO$_2$ loadings enhanced significantly by
119% and 43%, while the equivalent amount with NaX loading remained unchanged. The extraordinary performance in the presence of ZIF-8 particles was attributed to ZIF-8’s greater CO₂ adsorption capacity, adequate matrix compatibility, and larger hole diameter than CO₂ kinematic size.

In this study, we sought to improve the capability to separate CO₂/N₂ and CO₂/CH₄ by incorporating Ag-BTC particles into a novel Pebax TFN membrane. The use of Ag-BTC particles is the primary novel component of this research. Ag-BTC, a MOF belonging to the silver family, was selected due to its high CO₂ affinity (the abundance of –COOH moiety). The Ag-MOF framework would have high compatibility with the Pebax®1657 layer because hydrogen bonding between the H₃BTC and Pebax is encouraged. This is made possible by the organic ligand in the MOF skeleton. By inserting Ag-BTC particles in the Pebax®1657 skin layer and subsequently dip-coating the PEI sublayer, the TFNs were created. The physicochemical characteristics of the developed composite membranes were investigated using a variety of technical analyses. Gas permeation characteristics of all samples were appraised under dry and humidified conditions. The impacts of varying MOF content in combination with various gas pressures and temperatures on the CO₂ segregation of all samples were inspected and discussed in detail. To enhance the CO₂ separation efficiency in the thin Pebax layer of TFC membranes, Ag-MOF particles were here, for the first time, incorporated into the membrane.

2. Materials and methods

2.1. Chemicals

Pebax®1657, supplied by Arkema (Paris), included 60% PEO and 40% PA and was dried for one day at 80 °C before use. The support layer was made using PEI, which was acquired from Sigma-Aldrich. Silver(I) nitrate (AgNO₃) as the metal source, 1,3,5-benzene tricarboxylic acid (H₃BTC) as the organic ligand, methanol (MeOH) as the solvent, and potassium hydroxide (KOH) were acquired all from Merck for the synthesis of MOF. N-methyl pyrrolidone (NMP) was obtained from Sigma-Aldrich and utilized as a solvent for dissolving PEI polymer. Ethanol (99.8% purity, Merck) and DI water were employed as solvents (mixture of solvents) for Pebax®1657 powder. Acetone (99% purity) acquired from Merck was also used for the MOF’s washing stage. The Sabalan Co. (Iran) kindly supplied all of the gases used (i.e., CO₂, CH₄, and N₂) with a purity of 99.99% for the penetration tests.
2.2. Synthesis of Ag-BTC particles

The preparation of Ag-BTC particles was based on a known procedure [66-68], as sketched in Scheme 1. A stirring reaction technique of mixing the metal node and the organic linker source (at ambient temperature) was employed for the synthesis of Ag-BTC particles. Due to light sensitivity, all reactions were carried out in a dark chamber. In this regard, a solution of H$_3$BTC (0.21 gr, 1 mmol) in 20 mL MeOH was mixed with an aqueous solution of KOH (0.114 gr, 2 mmol) in 5 mL deionized H$_2$O. The mixture was agitated for several minutes to form a clear solution. A predetermined amount of AgNO$_3$ (0.34 gr, 2 mmol) was separately dissolved in 5 mL deionized H$_2$O and slowly added to the previously prepared solution. After 4 hours of stirring and reaching a uniform combination, the produced solution was settled in darkness at ambient conditions for (at least) 1 week. Few silvery particles were then attained. After ensuring the evaporation of the solvent and H$_2$O, the silvery solid materials were washed 3 times with acetone and again air dried for 3 days (yield: 0.425 gr (~65%)).

![Scheme 1. Ag-BTC synthesis rout](image)

2.3. Fabrication of PEI substrate

The polymeric PEI substrate was synthesized via a nonsolvent phase inversion approach. In terms of creating a molding solution with an acceptable fluidity, 10% of PEI was solubilized in 90% NMP. The mixture was then heated to 60 °C in an oil bath while being agitated mechanically for one day. A 150-micron thick cast knife was used to pour the homogeneous, bubble-free solution onto a polyester nonwoven fabric. After that, the molded film was placed in a deionized water reaction vessel to interchange solvents and nonsolvents. To prolong the phase inversion procedure over 2 days, the nonsolvent was changed with fresh water after an hour. The spongy PEI substrate was then left at room temperature for 24 hours to allow non-solvent drainage. The PEI substrate was ultimately dried for 18 hours at 60 °C in a vacuum oven to achieve maximum nonsolvent drying.
2.4. TFC/TFN membrane fabrication

To fabricate the TFC membrane, 5 wt.% of dried Pebax®1657 was first mixed with ethanol/water (70/30 wt.%) combination solvents at 60 °C for at least 150 min. The homogenized mixture was then cooled down to ambient conditions. After that, the previously synthesized PEI substrate was submerged for five minutes in the Pebax®1657 mixture. The solvent was then vaporized from the PEI/ Pebax®1657 TFC membrane by depositing it in a vacuum oven at 60 °C for 45 minutes. The aforementioned process was repeated multiple times to attain the skin layer necessary thick well over the PEI sublayer. Lastly, the finished TFC film was dehumidified at 60 °C for 12 hours.

According to the desired weight percentage (0.5, 1, 2, and 3 wt.%), predetermined amounts of Ag-BTC particles were suspended in solvent mixtures via ultrasonic irradiation (30 minutes) and stirring at 500 rpm (15 minutes) to avoid the accumulation of the MOF particles. The dried Pebax®1657 was then progressively added to the homogenously colloidal solutions. The final solutions were vigorously agitated for 3 hours at 60 °C. The coating process for the TFN membrane synthesis was the same as the pure TFC membrane. Table 1 lists the proportions of each dope solution including Pebax®1657 and Ag-BTC particles as well as the coating conditions.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Support layer (wt.%)</th>
<th>Selective layer composition (5 wt.%)</th>
<th>Solvent (wt.%)</th>
<th>Time of dip-coating (min)</th>
<th>Evaporation temperature (°C)</th>
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</thead>
<tbody>
<tr>
<td>PP</td>
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<td>100</td>
<td>95</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>PPG-0.5</td>
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<td>0.5</td>
<td>95</td>
<td>5</td>
</tr>
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<td>99</td>
<td>1</td>
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<td>97</td>
<td>3</td>
<td>95</td>
<td>5</td>
</tr>
</tbody>
</table>

2.5. Characterization methods

Attenuated Total Reflection Infrared (ATR-FTIR) spectroscopy (NICOLET iS10, USA) was used in the wavelengths of 600-4000 cm⁻¹ to inspect the formatted bonds and changes in composite membranes lattice. It should be noted that the Ag-BTC particles underwent FT-IR analysis between 400-4000 cm⁻¹. The N₂ adsorption isotherm of filler was also recorded (BELSORP, mini 2 Model, Japan) to obtain its porosity.
A Field Emission Scanning Electron Microscopy (FE-SEM) (MIRA3 TESCAN, Czech Republic) was utilized to analyze the structural characteristics of composite membranes in the vicinity of Ag-BTC particles and the quality of filler scattered throughout the Pebax®1657 lattice. The FE-SEM micrographs were taken up to a magnification of 50.00 kx. Moreover, the EDX profile and mapping analysis of the membranes were obtained using FE-SEM (Zeiss, Sigma 300-HV, Germany).

Thermal resistance and degradation temperature of Ag-BTC particles and nanocomposite films were appraised via thermo gravimetric analysis (TGA) (Mettler Toledo, USA) over temperatures between 0 and 600 °C at a pace of 10 °C/min in an N2 environment. A thermoanalytical technique was also employed to portray the phase transition of all samples (200 F3, Netzsch, Germany). In the present study, dual scanning DSC was accomplished in an N2 environment between -100 to 250 °C at a 10 °C/min scan rate.

2.6. Gas permeation experiment

The gas transport characteristics of the produced membranes were monitored using a variable pressure set-up system with an available mass transfer area of 15.25 cm². Pure and mixed gas permeation was assessed at temperatures of 30-50 °C and the input pressures of 2-10 bar (pure N2, CH4, and CO2 gases and mixed gases of CO2/CH4 with 50:50 v/v and CO2/N2 with 15:85 v/v). Mixed gases were additionally humidified with water to assess the removal efficiency in moist settings. In-depth details on performance evaluation can be found in the supplementary file. The specifications of the used gases are given in Table 2.

<table>
<thead>
<tr>
<th>Penetrant</th>
<th>Kinetic diameter (Å)</th>
<th>Critical temperature (°K)</th>
<th>Condensability (°K)</th>
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</thead>
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<td>304.550</td>
<td>195</td>
</tr>
<tr>
<td>N2</td>
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<td>126.192</td>
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<tr>
<td>CH4</td>
<td>3.80</td>
<td>190.550</td>
<td>149</td>
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</tbody>
</table>

3. Results and discussion

3.1. Characterization of Ag-BTC particles

The FT-IR spectrum of the fabricated Ag-BTC particles is illustrated in Fig. 1(a). Four middle strong peaks at 519, 670, 704, and 743 cm⁻¹ point to vibrations of Ag–O, which reflect successful coordination between Ag⁺ and –COOH moiety of the BTC linker [69]. The peaks that appeared in
the frequency interval 800-1255 cm\(^{-1}\) and 2399-3122 cm\(^{-1}\) are consistent with the C–H bending vibration and the C–H stretching vibration of the aromatic ring of the BTC linker, respectively [66, 70, 71]. The absorption peak of the C–C bond is observed at 1107 cm\(^{-1}\). The strong peak at 1358 cm\(^{-1}\) also indicates the C–O stretching vibration in the Ag-BTC skeleton [69]. Strong absorption bands of –COOH moiety emerging at 1513 and 1546 cm\(^{-1}\) are attributable to the symmetric stretching vibration of the linkage between C–O and Ag (COOM), and the asymmetric C=O stretching vibration of the BTC linker and Ag ion (COOM) is measured at 1607 and 1683 cm\(^{-1}\) [72-74], authenticating the bridged coordination modes of –COOH moiety. Moreover, the relatively weak bands in the 2550-3060 cm\(^{-1}\) region with varied intensities are associated with the –OH stretching vibration in –COOH groups [72]. The –OH moiety (H\(_2\)O) is typically credited with the broad peak in the frequency region of 3330-3580 cm\(^{-1}\).

The morphology of synthesized Ag-BTC was explored by the FE-SEM test. As shown in Fig. 1(b), Ag-BTCs have a regular structure with a bunch of nano-fibrous appearances; as their length varied from \(~0.5\) to 2 \(\mu\)m. The \(\text{N}_2\) adsorption-desorption isotherm of fabricated Ag-BTC is also illustrated in Fig. 2(c). The Brunauer–Emmett–Teller (BET) surface area is about 5.80 m\(^2\).g\(^{-1}\), total pore volume is \(~0.02\) cm\(^3\).g\(^{-1}\) (\(p/p_0=0.984\)), and the average pore diameter is 6.15 nm, showing a mesoporous structure.

The thermal stability of the synthesized compound was inspected through TGA; the resulting findings are shown in Fig. 1(d). It would seem that the Ag-BTC particle has appropriate thermal stability at \(~275\) °C in atmospheric air. Regarding the thermogram, the Ag-BTC particle experiences a three-stage weight loss. The primary weight loss of 3% up to 275.40 °C refers to the departure of the coordination water molecules and guest solvent molecules trapped in the pores. The significant weight loss of 55.67% between 275.40-400.33 °C is ascribed to the degradation of BTC linkers. The tertiary part indicates the formation of oxide (\(i.e.,\), Ag\(_2\)O, AgO) [68, 74]. At higher temperatures (>400), oxides are gradually decayed to release oxygen, therefore, a steady downward trend has emerged. Lastly, the remaining residue was approximately 38\%.
Fig. 1. Ag-BTC analysis: (a) FTIR spectrum, (b) FE-SEM image, (c) BET analysis at 196 °C, and (d) TGA curve.

3.2. Characterization of nanocomposite membranes

3.2.1. ATR-FTIR evaluation

Fig. 2 illustrates the diagram of ATR-FTIR of the fabricated membranes. As it is conspicuous, there are six marked peaks at ~848, ~1096, ~1637, ~1733, ~2868-2938, and ~3298 cm\(^{-1}\) for the neat Pebax\textsuperscript{®}1657, which are consistent with earlier research [1, 75-80]. The absorption band at ~848 cm\(^{-1}\) for the pure film denotes the stretching vibrations of the –OH moiety [75, 79]. The bands absorbed in ~1096 and ~1733 cm\(^{-1}\) are associated with the C–O–C tensile vibrations in the ether moiety of the PE block and the C=O moiety in the PA block, respectively [1, 80]. The absorption bands at the frequency interval ~2868-2938 cm\(^{-1}\) would also correlate to the C–H
functionalities. The amide moiety and N–H functionality in the PA phase, respectively, are represented by the distinctive bands at ~1637 and ~3298 cm\(^{-1}\) [75, 81].

Upon the incorporation of Ag-BTC particles, no new absorbance peaks were observed for composite membranes, revealing the physical blending between the filler-Pebax®1657. The addition of filler not only decreased the intensity but also shifted the absorption bands to a lower frequency. The peaks moved slightly to the right owing to the mutual interactions among the polymer and filler. As seen in Fig. 2, the stretching vibrations of the N–H group transferred from 3297.67 cm\(^{-1}\) to 3296.20 and 3295.06 cm\(^{-1}\) for MMM containing 1 and 2 wt.% Ag-BTC, respectively. For the amide group, a migration from 1637.27 cm\(^{-1}\) for the pure film to 1636.39 and 1635.42 cm\(^{-1}\) for MMM containing 1 and 2 wt.% filler was observed. The peak at 848.53 cm\(^{-1}\) belonging to –OH moiety also experienced a move to the right to 844.13 and 842.65 cm\(^{-1}\) for 1 and 2 wt.% filler loading. Other peaks did not change intensively or indicated the same frequency, which could be due to the relatively small amounts of Ag-BTC particles.

The reduced intermolecular H–bonds between the PE and PA phases in the neat Pebax®1657 and the subsequent development of novel H–bonds among the functional groups of Pebax®1657 and Ag-BTC particles may be the cause of these minor modifications [82]. Scheme 2 provides additional clarification on the potential intermolecular interaction process in composite membranes.

![Fig. 2. FTIR-ATR spectra of composite membranes: (a) Pure Pebax®1657, (b) Pebax/Ag-BTC (1 wt.%), and (c) Pebax/Ag-BTC (2 wt.%).](image-url)
Scheme 2. Representation of intermolecular interaction between Pebax®1657 and Ag-BTC particles.

3.2.2. Morphological study

One of the key factors in the MMM that affects significantly the gas transport capabilities is the degree of fillers’ distribution inside the polymeric matrices. Regarding this issue, the crossing and surface morphology of the TFC/TFN films were studied utilizing FE-SEM imaging. Fig. 3 exhibits the FE-SEM cross-sectional images and top views of as-synthesized membranes. As can be seen, the skin film is well-inhered on the PEI sublayer and shapes a border without cracks. While a thick film of about 140 µm with a sponge-type structure for the PEI substrate is observed, the Pebax®1657 top dense layer possesses a much lower thickness of around 3–3.5 µm, indicating a thin permeable/selective layer suitable for CO2-relevant separation.

Referring to Fig. 3, the embedment of Ag-BTC particles in the structure of neat Pebax changed the smooth cross-sections of composite membranes and the membranes lost their even patterns (the so-called grooved pattern) emerging from the favorable interactions between the polymer chains and filler’s functional groups (i.e., carboxyl). The cross-section micrographs also illustrate a crack-free and uniform structure, which could be a sign of excellent adaptability among components. In addition, the surface morphology of composite films reveals appropriate dissemination of nanosized Ag-BTC particles in the polymer lattice. The consistent theme without any structural flaws reveals a proper processing route and also the meticulous drying procedure during the production of the films. The pre-sonication step also contributed to better Ag-MOF
particle distribution. This step further caused the nano-fiber bundles to be converted into smaller fiber segments with sizes between ~20-70 nanometers. After being sonicated in the solvent combination, the length of the particles was reduced. These findings support the assertion that the nanomaterials are sufficiently small in such a way that their integration into the membrane's selective layer would not cause defects (Fig. 3-top surface).

Good/favorable interactions between Pebax®1657 chains and Ag-BTC particles effectively prevented the generation of non-selective pinholes at the interfacial region, which led to intensely desirable permselectivity results. Nonetheless, some degrees of MOF accumulation can be observed in some parts of the fabricated membranes (i.e., PPG-3). The reason behind these few agglomerations could be the large difference between the surface energy of polymers and nanofillers [82]. Others have noticed this behavior, above certain filler content levels [55, 83, 84].
Fig. 3. FE-SEM images of composite membranes: top layer (left), cross-section (middle), and the top surface (right).
EDX analysis was used to confirm the existence of Ag-MOF in the membranes’ lattice. The obtained results of EDX analysis for the neat Pebax1657, Pebax/Ag-BTC-0.5, Pebax/Ag-BTC-1, and Pebax/Ag-BTC-2 are displayed in Fig. 4. The detected silver (Ag) in Figs. 4(b-d) confirmed the existence of Ag-MOF within the Pebax1657 matrix. In addition, the mapping analysis (Figs. 4(b-d)) of MMMs indicated appropriate dispersion of Ag-BTC throughout the Pebax network.

![Fig. 4](image-url). EDX profile and mapping analysis of the neat pebax1657 (a), Pebax/Ag-BTC-0.5 (b), Pebax/Ag-BTC-1 (c), and Pebax/Ag-BTC-2 (d).

3.2.3. Thermal properties of Pebax/Ag-BTC

TGA was utilized to survey how Ag-BTC particles modified the durability of fabricated Pebax/Ag-BTC nanocomposites and the obtained results are reported in Fig. 5(a). The thermal
degradation temperature \( (T_d) \) of all nanocomposites was also evaluated by TGA. As it is conspicuous, the losing weight profile of samples involves a three-distinct-steps, specifically, prior to decomposition (residue guest solvent evaporation), degradation and destruction region (depolymerization), and damping area (carbonization), at about 50-150, 350-500 and 500-600 °C, respectively. The pristine membrane exhibited excellent thermal stability. It indicated a \( T_d \) of about 360 °C associated with polymer degradation. But the thermal decomposition was slightly reduced for the prepared nanocomposite membranes, which could be attributed to the lower thermal stability of Ag-BTC particles in comparison with the pure Pebax membrane, as observed for UiO-66-NH\(_2\)-incorporated Pebax®1657 membrane [55]. Moreover, regarding Fig. 5(a), the remaining weight of fabricated membranes was approximately 2, 6, and 8 wt.% for the pristine membrane, Pebax/Ag-BTC-1 wt.%, and Pebax/Ag-BTC-3 wt.%, respectively.

DSC analysis was performed on all samples to scrutinize the glass transition temperature \( (T_g) \) and variations in crystallization of fabricated Pebax/AgBTC nanocomposites. The results have been sketched in Fig. 5(b) and tabulated in Table 3. As can be noticed, each sample has 2 significant crystalline areas. One is an endothermic apex from the PE soft block that ranges from 5 to 35 °C. The latter began to occur at 170-230 °C and is connected to crystallization within the PA rigid block.

Referring to Table 2, the \( T_g \) of neat Pebax and Pebax/Ag-BTC 3 wt.% are detected at -51.10 °C and -42.70 °C, respectively. This indicates that the \( T_g \) of samples increased as a result of the Ag-BTC particles being embedded in the polymer network \( (\Delta T=8.40 \text{ °C} \text{ for the highest content respecting the bare Pebax}) \). Upon the insertion of MOF in the Pebax lattice, robust interactions and chemical crosslinking among the hydroxyl and carboxyl moieties on the Ag-BTC surface and available functional moieties of both (PE/PA) segments take place so that the free molecular movement of the chains is constrained.

The degree of crystallinity of nanocomposite membranes was assessed using Eq. (4) [85]:

\[
X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100
\]

where \( X_c \) is the crystallinity percent of the singular sample, \( \Delta H_f^0 \) (J.g\(^{-1}\)) refers to the heat fusion of the membrane at the state of 100% crystallinity (denoted by the superscript 0). The values of \( \Delta H_f^0 \) are of 233 J.g\(^{-1}\) and 166.4 J.g\(^{-1}\) for the PA and PE segments, respectively [85]. \( \Delta H_f \) (J.g\(^{-1}\))
represents the enthalpy of fusion of each membrane computed by integrating the area under the melting peaks.

The total crystallinity \( (X_{tc}) \) of the fabricated films (based on Pebax®1657) was also estimated using Eq. (5) as follows:

\[
X_{tc} = 0.6X_{PE,crystallinity} + 0.4X_{PA,crystallinity}
\]  

According to Table 3, the measured crystallinity of nanocomposite membranes declined compared to the pristine membrane and further decreased with more loading of Ag-BTC particles. The Ag-BTC filler led to a great interruption to the arrangement of chains of the Pebax polymer, which lowered the crystallinity degree. More importantly, the small size of the Ag-BTC filler resulted in a uniform distribution within the Pebax®1657 matrix and enormously exacerbated the situation.

### Table 3

The \( T_g \), melting point, energy required for the dissociation of bonds, and crystallinity degree of each PU membrane

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g(\degree C) )</th>
<th>( T_{m,PE} ) ( (^\circ C) )</th>
<th>( T_{m,PA} ) ( (^\circ C) )</th>
<th>( \Delta H_{f,PE} ) ( (J.g^{-1}) )</th>
<th>( \Delta H_{f,PA} ) ( (J.g^{-1}) )</th>
<th>( X_{PE} )</th>
<th>( X_{PA} )</th>
<th>( X_{tc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>-51.20</td>
<td>16.80</td>
<td>207.40</td>
<td>29.20</td>
<td>77.30</td>
<td>0.175</td>
<td>0.336</td>
<td>23.972</td>
</tr>
<tr>
<td>PPG-0.5</td>
<td>-49.70</td>
<td>18.10</td>
<td>204.20</td>
<td>28.20</td>
<td>73.60</td>
<td>0.169</td>
<td>0.320</td>
<td>22.968</td>
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<tr>
<td>PPG-1</td>
<td>-46.80</td>
<td>19.40</td>
<td>203.30</td>
<td>27.50</td>
<td>68.40</td>
<td>0.165</td>
<td>0.297</td>
<td>21.812</td>
</tr>
<tr>
<td>PPG-2</td>
<td>-44.20</td>
<td>21.20</td>
<td>202.60</td>
<td>26.20</td>
<td>65.20</td>
<td>0.157</td>
<td>0.283</td>
<td>20.876</td>
</tr>
<tr>
<td>PPG-3</td>
<td>-42.70</td>
<td>23.60</td>
<td>201.10</td>
<td>25.60</td>
<td>60.70</td>
<td>0.154</td>
<td>0.264</td>
<td>19.787</td>
</tr>
</tbody>
</table>

![Fig. 5](image_url) The TGA curve (a) and DSC thermogram (b) of neat Pebax®1657 and MMMs.
3.3. Gas separation efficiency

Permselectivity of the produced membranes (TFC and TFNs) was determined at a broad range of temperatures (30-50 °C) and pressures (2-10 bar). Various percentages of Ag-BTC particles (0, 0.5, 1, 2, and 3 wt.%) were added to the matrix to evaluate the impacts of applying the filler on the neat TFC’s ability to separate gases. The results are comprehensively discussed below.

3.3.1. Transport parameter of pure gas
3.3.1.1. Effects of Ag-BTC loadings

The permeation rates of the fabricated films were appraised at various Ag-BTC loadings (0, 0.5, 1, 2, and 3 wt.%) under varied feed pressures up to 10 bar at 30 °C. Fig. 6 reveals the effect of the addition of Ag-BTC particles on the permeability of gases through Pebax1657 membranes at an input pressure of 4 bar.

At first glance, it can be found that the Ag-BTC particles’ presence improved the prepared membrane’s gas transport properties. The simultaneous increment in CO₂ gas permeation and its relative selectivities could be associated with the increase of additional transport channels, open/unsaturated Ag⁺ sites, the mutual interactions of Ag-BTC filler and CO₂, the increase of CO₂ solubility in the presence of polar moieties (i.e., carbonyl and hydroxyl groups) in fabricated composite membranes, and a disturbance in chains packaging via Ag-BTC nanoparticles [55, 64].

This clearly demonstrates that the Ag⁺– CO₂ interaction, which increases solubility, is the cause of the rise in CO₂ permeability. This was consequently verified by measuring the solubility coefficient as a function of the filler content, which was established, for instance, by measurements of the time-lag of self-standing membranes (MMMs) (eqs. S5 & S6). The outputs are presented in Fig. S1. Although the diffusivity coefficient of gases increased with the increase of Ag-BTC concentration, all diffusivity selectivity \(D_{\text{CO}_2}/D_{\text{CH}_4}\) values for the synthesized MMMs are lower than those for the pure Pebax1657. On the other hand, solubility selectivity \(S_{\text{CO}_2}/S_{\text{CH}_4}\) and \(S_{\text{CO}_2}/S_{\text{N}_2}\) increased by increasing Ag-BTC loading. Compared to the neat Pebax1657, all MMMs have higher solubility selectivity because of the impressive CO₂ sorption by the filler. It is important to notify that the Ag-BTC filler in MMM separate gases based on preferential adsorption of CO₂, not size sieving. Consequently, this phenomenon led to the more solubility selectivity of MMM compared to the pure Pebax1657. Moreover, the appropriate compatibility among the
Pebax polymer and Ag-BTC filler, as proved by FE-SEM images, could effectively reduce the non-selective permeation, improving both ideal selectivities.

For all evaluated penetrants, the TFN films’ permeability moved upwards. That whole, after inserting Ag-BTC particles in the membrane's architecture, may be mainly due to the inherent nanofiller permeance as well as the enhanced FV of the Pebax lattice. In comparison to CH₄ and N₂ gases, the CO₂ permeability became noticeably higher across all prepared samples, which was ascribed to the smaller core diameter of CO₂ (3.30 Å for CO₂ versus 3.64 Å for N₂ and 3.80 Å for CH₄) and the CO₂ better condensability than CH₄ and N₂ gases that led to a stronger gas solubility inside the films. Additionally, the high polarity of the bonds in the CO₂ molecule (even though CO₂ is a nonpolar gas, the polarity of its single C=O bond provides fertile ground for intense interactions with other materials’ polar functionalities) allowed a strong electron interaction with high polar groups of the Ag-BTC particles (i.e., carboxyl moiety), thereby this high affinity facilitated greatly the absorption of CO₂. Furthermore, the mutual interaction between reactive CO₂ and the PA amide moiety (i.e., H-bondings) intensified the carbon dioxide penetration [55]. To shed light on this, at 4 bar, the rates of CO₂ penetration were 14.82, 15.12, 15.77, 16.74, 29.92 times higher than CH₄ values and 26.67, 26.94, 27.98, 29.92, and 31.74 times higher than N₂ amounts within PP, PPG-0.5, PPG-1, PPG-2, and PPG-3, respectively.

![Graph](image)

**Fig. 6.** The effect of Ag-BTC content on gas permselectivity at a feed gas pressure of 4 bar.

3.3.1.2. Effects of feed gas pressure

Fig. 7 illustrates how well the TFC/TFN films separate CO₂/CH₄/N₂ at various pressures from 2-10 bar at a specific temperature (30 °C). The permeation graphs disclose an ascending pattern for all gases as the input pressure rises to 10 bar. While the CO₂ experienced a steep rise in
permeation values, CH₄ and N₂ increased moderately, thereby the gas pair selectivities increased continuously. Accordingly, the magnitude of the gases’ permeability follows the order: 

CO₂>>>CH₄>N₂

A greater penetration rate for CO₂ was anticipated since the carbon dioxides used the pairing of adsorption and condensation mechanisms to move across the membranes. For example, the permeability of CO₂ for PPG-2 increased from 213.00 to 360.20 Barrer with rising pressure from 2 to 10 bar, while the comparable numbers for CH₄ and N₂ could be 13.35 to 17.14 Barrer and 7.39 to 9.78 Barrer, respectively.

At greater input pressures, the Pebax matrix’s content of reactive CO₂ enhanced, which led to a plasticization-induced rise in permeability. In addition, the constructed TFC/TFN films were far more capable of carrying CO₂ over light penetrants because of the coordinatively free silver's attraction (Ag⁺) to CO₂ molecules, which have potent quadrupole moments. Further, the CO₂ sorption by Ag-BTC MOF increased at elevated feed pressure, which significantly improved the permeability of CO₂ gas. What is more, allocating the smallest molecular size coupled with the highest condensability resulted in a greater CO₂ permeation rate compared to the large and non-condensable penetrants. All in all, these points significantly helped to offset the reduction in CO₂ transportation brought on by the compaction of the polymer chains, and consequently, the gas pair selectivities increased gently.

As long-term stability is considered the epitome feature of membranes intended for utilization in industries. To demonstrate the long-term durability, the Pebax composite membrane (i.e., PPG-2) was exposed to the pure gas form at 6 bar and 30 °C for extended periods of time. The outcomes are shown in Fig. S2. During this testing, the composite membrane performance was relatively stable for a prolonged time of 12 days. The CO₂ permeability and its relative selectivities remained unchanged in the timescale studied. Although the CO₂ permeability reduced by 4% from 279.49 to 267.90 Barrer, the CO₂/CH₄ and CO₂/N₂ separation factors were stood at around 17.5 and 32, respectively, similar to the fresh membrane. It demonstrates that Ag-BTC could maintained its structure and properties under the test conditions, suggesting a good potential in practical CO₂ separation applications.
Fig. 7. The effect of pressure changes on permeability and gas pair selectivities.
3.3.1.3. Effects of operating temperature

The separation efficiency of the TFC/TFN films is displayed in Fig. 8 as a function of Ag-BTC loading at various temperatures. As expected, the permeability of gases increased with the operating temperature. As the operating temperature rises, the flexibility and dynamic of polymer chains increase, and tortuous mode becomes the dominant phenomenon. Consequently, the fraction of FV in the polymer matrix increases, leading to increased diffusivity [83, 86]. Therefore, a great permeability increment with temperature for CH$_4$ and N$_2$ large gases could be expected.

As long as the free volume increases, the penetration of larger molecules is facilitated. Referring to Table 2, although CH$_4$ has a larger molecular diameter in comparison with N$_2$, N$_2$ possesses a higher permeability enhancement. This behavior is related to the higher condensability of CH$_4$, which leads to lower solubility when the temperature rises. Owing to a lack of significant impact on its solubility, N$_2$ shows a larger increase in permeability respecting CH$_4$ [86]. According to the findings, the permeability increase of penetrants through the Pebax membranes obeys the following sequence:

CO$_2$ < CH$_4$ < N$_2$

It shows that both separation factors would reduce that because the CO$_2$ molecule has the smallest kinetic size. Enhancing the operating temperature increases the chain mobility and produces more free volume; subsequently, the molecular sieving effect is reduced. For instance, the CO$_2$ permeability for PPG-3 increased from 321.34 to 360.00 Barrer when the temperature was raised from 30 to 40 °C, whereas the CO$_2$/N$_2$ and CO$_2$/CH$_4$ factors reduced by ~19% and ~12%, respectively.

The van't Hoff-Arrhenius model explains how temperature affects the permeability of gases:

\[ P = P_0 \exp(-E_p/RT) \]  

where $E_p$ refers to the penetration activation energy determined out of a logarithmic $P$-$T^{-1}$ diagram [kJ. mol$^{-1}$]. $P_0$ indicates the temperature-independent pre-exponential factor presented in Barrer. $T$ and $R$ also represent the absolute temperature (K) and the gas constant (kJ. mol$^{-1}$. K$^{-1}$), respectively.

The $E_p$ for all tested gases was calculated and the obtained data is depicted in Fig. 9 and listed in Table 4. The computed $E_p$ ratios for CO$_2$ may be seen to be lower than for other gases. The lower $E_p$ the higher the permeability, therefore, CO$_2$ shows higher permeability respecting the
other gases tested as the temperature rises. Noteworthy, the $E_P$ values of all gases are decreased with enhancing filler loading, confirming the permeation results where higher permeability amounts are obtained as the Ag-BTC content increases.

Fig. 8. The Effect of temperature on gas permeability and permselectivity of the fabricated membranes at 6 bar.

Fig. 9. Permeation activation energy for CO$_2$.

| Table 4 |
| The $E_P$ (kJ. mol$^{-1}$) for all penetrants at a pressure of 6 bar |
|----------|---------|---------|---------|---------|---------|
| Sample  | PP      | PPG-0.5 | PPG-1   | PPG-2   | PPG-3   |
| Gas     |         |         |         |         |         |
| CO$_2$  | 11.98   | 11.54   | 10.00   | 9.16    | 8.81    |
| CH$_4$  | 21.89   | 20.70   | 19.45   | 18.93   | 17.86   |
| N$_2$   | 27.81   | 25.93   | 24.43   | 23.19   | 21.56   |
3.3.2. Transport parameter of mixed gas

The constructed TFC/TFN films' ability in separating dry and humid mixed gases (15:85 v/v of CO$_2$/N$_2$ and 50:50 v/v of CO$_2$/CH$_4$) was validated at gas pressures from 2-10 bar at constant temperature (30 °C).

Gas combinations were passed through the manufactured membranes, and the permeable flow was then transmitted to a GC device to identify the content of the gas. Figs 10, S3, and S4 are sketches of the results that were achieved. It can be found that the pattern of variations in permselectivity for mixed gas is roughly comparable to those of the single gas, with a sharp increase in CO$_2$ penetration but a fair increment in the permeability of light gases, and subsequently a continual increase in gas pair selectivities. For instance, while the CO$_2$ permeability for the PPG-2 membrane increased by ~83% (dry-mixed gas state), the permeability of CH$_4$ enhanced by ~28% with rising pressure from 2 to 10 bar, therefore, the separation factor increased substantially.

As might be predicted, the real selectivities and gas permeabilities are lower than the pertinent figures for the permeability and selectivity of single gases. As an illustration, at an inlet pressure of 8 bar, the CO$_2$ permeability of PPG-3 declined by 32% from 372.00 Barrer for single gas to 253.03 Barrer for dry-mixed stream. The CO$_2$/CH$_4$ ideal selectivity was 20.42, while the corresponding value for mixed gas dropped to around 19. This reduction in values certainly refers to CH$_4$ and N$_2$ non-polar molecules in the gas mixtures. This presence not only causes a competitive permeation through the Pebax selective layer but also these molecules can occupy the FV of the polymer, thereby reducing the CO$_2$ sorption and condensation [64, 83]. Because of its great propensity to solubility mechanism, CO$_2$ gas experienced a noticeable decrease in permeation rate, while CH$_4$ and N$_2$ gases gradually declined concerning their pure values. It can be also seen that the insertion of Ag-BTC particles in the Pebax thin layer greatly improved the ability of membranes to segregate CO$_2$. Further increment of Ag-BTC loading to 3 wt.% resulted in higher CO$_2$ permeability and subsequently greater CO$_2$/N$_2$/CH$_4$ selectivity. As mentioned earlier, due to the extra transport channels and the strong attraction of the free Ag$^+$ sites towards CO$_2$ molecules, a higher CO$_2$ penetration rate can be expected.

In comparison with the dry conditions, the permeability of penetrants and their relative selectivities increased under a humid state. In the humidified condition, with an applied pressure of 8 bar, the PPG-3 membrane's CO$_2$ permeability and CO$_2$/CH$_4$ selectivity enhanced from 253.03 Barrer and 19.01 in the dry condition to 290.40 Barrer and 20.03. In the presence of water,
Pebax®1657 exhibits a greater CO₂ selectivity against other species (i.e., CH₄, N₂). Gas permeability, particularly for tiny and condensable CO₂ gas, increases as a result of hydrophilic Pebax's capacity to catch and maintain water molecules within its polymer chains [12, 87]. Given the fact that the Pebax-based membrane is a water-swellable polymer (WSP), additional types of CO₂, like HCO₃⁻, can pass through it quickly and selectively. As a consequence of that, the permeation of CO₂ is made easier in humid environments [55]. Referring to the results depicted in Figs 10, S3, and S4, although the existence of CH₄ and N₂ molecules barricaded the passing of CO₂ through the membranes, the constructed TFC/TFN films still delivered a fine performance for carbon capture and sequestration.

![Graph 1]  ![Graph 2]

**Fig. 10.** Mixed gas performance of different membranes under dry and humid conditions at 30 °C and 6 bar.

### 3.3.3. Functionality of constructed films

The capability of Pebax-based TFC membranes filled with various MOFs for CO₂/CH₄/N₂ separation is presented in Table 5. It is almost tangible that the separation functionality of TFN films is a strong function of MOFs’ type used and the working circumstances (e.g., p and T). It can be noticed that the established conflict between permeability and selectivity can be conquered via the impregnation of membranes with potential fillers. As represented, the TFN membranes developed in this study delivered superior permeability and selectivity. Compared to previously released work, the Pebax-Ag-BTC/PES TFN membranes (even with small quantities of Ag-MOF) express almost higher permeability coupled with a sufficient range of separation factors.

Fig. 11 displays the results of evaluating the separation efficiency of manufactured TFC/TFN films for pure gas using the Robeson market principle. It can be noticed that the evolution of all constructed films deviates from the essence of the famous trade-off (low selectivity accompanied
by high permeability, and conversely). It is conspicuous that the embedded Ag-BTC in PP and higher feed pressure improve CO₂ separation. CO₂/N₂ separation performance got close to the present line. CO₂/CH₄ separation advanced continuously and crossed the prior line at 8 and 10 bars for the PPG-3 membrane. To sum up, the presence of amide moiety in the Pebax matrix, the extra FFV upon the addition of fillers, the high tendency of free Ag⁺ toward CO₂, more condensability of CO₂, and higher feed pressure were the determining factors influencing the ability of Pebax composite films to overcome the Robeson upper bound.

Table 5
The comparison of CO₂/CH₄ and CO₂/N₂ separation performance of Pebax-based TFN membranes with the experimental data obtained in this work.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler (wt.%)</th>
<th>Test condition (T(°C)/p(bar))</th>
<th>P_{CO2} (Bar)</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSI/PTMSP/Pebax renew 30R51</td>
<td>–</td>
<td>35/3</td>
<td>497</td>
<td>27</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>IL a (10)</td>
<td></td>
<td>629</td>
<td>29</td>
<td></td>
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<tr>
<td></td>
<td>IL (10)-ZIF-8 (15)</td>
<td></td>
<td>751</td>
<td>25</td>
<td></td>
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<td></td>
<td>IL (10)-ZIF-94 (15)</td>
<td></td>
<td>819</td>
<td>25</td>
<td></td>
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<tr>
<td>PES/Pebax1657</td>
<td>TEPA-MIL-101b (5)</td>
<td></td>
<td>34.60</td>
<td>46.33</td>
<td>–</td>
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<td></td>
<td>TEPA-MIL-101 (5)</td>
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<td>35.10</td>
<td>37.11</td>
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<tr>
<td></td>
<td>TEPA-MIL-101 (7.5)</td>
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<td>31.30</td>
<td>35.93</td>
<td></td>
</tr>
<tr>
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<td>Ni-NH₂-BDC (0)</td>
<td>20/6</td>
<td>19.05</td>
<td>32.19</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Ni-NH₂-BDC (5)</td>
<td></td>
<td>31.55</td>
<td>94</td>
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<tr>
<td>PVDF/PTMSP/Pebax1657d</td>
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<td>25/2</td>
<td>225e</td>
<td>15</td>
<td>43</td>
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<tr>
<td></td>
<td>ZIF-8 (30)</td>
<td></td>
<td>350e</td>
<td>13</td>
<td>31</td>
</tr>
<tr>
<td>PMP/Pebax1657</td>
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<td>369.30</td>
<td>31.30</td>
<td>–</td>
</tr>
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<td>UiO-66-NH₂ (1.5)</td>
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<td>393.40</td>
<td>39.80</td>
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<td></td>
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<td></td>
<td>231.70c</td>
<td>20.30</td>
<td></td>
</tr>
<tr>
<td>PES/Pebax1657</td>
<td>ZIF-8 (0)</td>
<td>25/4</td>
<td>51.50</td>
<td>–</td>
<td>61.53</td>
</tr>
<tr>
<td></td>
<td>ZIF-8 (2)</td>
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<td>112.65</td>
<td>108.20</td>
<td></td>
</tr>
<tr>
<td>PAN/Pebax1657</td>
<td>MOF-801 (7.5)</td>
<td>20/1</td>
<td>22.40c, e</td>
<td>–</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>43c, e, h</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>
Table 4. Comparison of the performance of the fabricated membranes and the literature data presented in Table 5 with Robeson’s upper bound at different pressures.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Ag-BTC Type</th>
<th>FV</th>
<th>CO2 Permeability (Barrer)</th>
<th>CO2/N2 Selectivity</th>
<th>CO2/CH4 Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN/PTMSP/Pebax1657</td>
<td>ZIF-7 (0)</td>
<td>20/3.75</td>
<td>72</td>
<td>14</td>
<td>34</td>
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<tr>
<td></td>
<td>ZIF-7 (8)</td>
<td>145</td>
<td>23</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZIF-7 (22)</td>
<td>111</td>
<td>30</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>PES/Pebax1657</td>
<td>Ag-BTC (0)</td>
<td>30/8</td>
<td>202.20</td>
<td>16.70</td>
<td>29.82</td>
</tr>
<tr>
<td></td>
<td>Ag-BTC (1)</td>
<td>268.10</td>
<td>18.62</td>
<td>32.30</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Ag-BTC (3)</td>
<td>372.00</td>
<td>20.42</td>
<td>36.76</td>
<td></td>
</tr>
</tbody>
</table>

a: [Bmim][BF4] ionic liquid (IL), b: a post-synthesis modification method was used to graft tetraethylenepentamine (TEPA) on MIL-101(Cr), c: mixed gas, d: hollow fiber, e: GPU, f: humid state, g: in situ growth of UiO-66-NH2 on the exterior surface of carbon nanofibers (CNFs), h: at 60 °C.

Fig. 11. Comparison of the performance of the fabricated membranes and the literature data presented in Table 5 with Robeson’s upper bound at different pressures.

4. Conclusion

The synthesized Ag-BTC particles were embedded in the Pebax®1657 skin layer to prepare TFN films with excellent gas permeation characteristics in this work. According to the characterization experiments, Ag-BTCs were spread evenly throughout the Pebax lattice, which minimized the likelihood that non-selective vacancies would occur in the interfacial region. Ag-BTC particles were discovered to massively raise CO2 permeability in the Pebax medium. Increasing the FV of composite membranes coupled with the high affinity of Ag-BTC filler to adsorb condensable CO2 resulted in elevated CO2 permeability and solubility rate. Contrary to CO2, the enhanced diffusivity coefficients of N2 and CH4 improved the gas permeability slightly, leading to a significant increment in CO2/N2 and CO2/CH4 selectivities. In addition, the permeability and selectivity of synthesized TFC/TFN films enhanced concurrently with the rise in
inlet pressure. By increasing the pressure from 2 to 10 bar, the permeability of CO\textsubscript{2} for PPG-3 increased from 235.27 to 394.97 Barrer, and as a result, the CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} selectivities rose by \(~\)25\% and \(~\)28\%, respectively. Moreover, for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} mixed streams in dry and humid states, the real selectivity and CO\textsubscript{2} permeability of the synthesized TFC/TFN films were enhanced.

The PES/Pebax-Ag-BTC TFN membranes that were created had amazing characteristics that followed the same pattern in permeability and selectivity. This characteristic, when combined with a greater inlet pressure varying from 2-10 bar, made it easier for the TFN membranes to approach Robeson's restriction. Comparable to the TFC membrane, the CO\textsubscript{2} permeability and selectivities of TFN membranes (e.g., PPG-3) developed in the present work were noticeably enhanced. Overall, it sounds like the Ag-BTC MOF will work well as a nanofiller to embed in the Pebax-based-TFC membranes for CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} sequestration.

Credit authorship contribution statement

Mohammad Hadi Nematollahi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. Pedro J. Carvalho: Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration. João A. P. Coutinho: Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. Reza Abedini: Conceptualization, Methodology, Validation, Data curation, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declaration of Competing Interest:

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Highlights

- Fabricating new TFN membranes by mixing Pebax®1657 and Ag-BTC particles
- The presence of Ag-BTC particles improved the gas transport properties
- Gas permeance and selectivity increased with the filler content, especially for CO₂
- Mixed gas test also showed a similar trend but lower values than a pure one
- The permeance rate was increased in the presence of water