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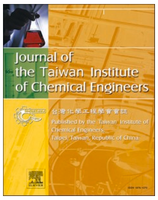

High-performance [EMIM][Tf₂N]-grafted silica/polysulfone hybrid membranes for enhanced CO_2/CH_4 separation: An experimental and computational approach

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ABSTRACT

Background: Mixed matrix membranes (MMMs) containing three components consisting of a polymeric continuous phase, a solid inorganic material, and an ionic liquid are widely explored for CO_2 removal from natural gas to increase energy content, reduce corrosion, and enable safer utilization. However, most of the previous studies have relied on physically blended or impregnated ionic liquids (ILs), which suffer from leaching and membrane instability, ultimately limiting their separation performance. Moreover, experimental methods alone cannot fully explain gas transport mechanisms or interactions between polymers, fillers, and gases with sorption sites.
Methods: This work employs a grafting strategy to covalently support 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) onto silica surface (IL-Si), ensuring long-term stability, uniform dispersion, improved compatibility between polymer and filler, and enhanced gas separation performance. Hybrid membranes with filler contents ranging from 5 to 20 wt.% were experimentally fabricated and analysed from an atomistic perspective using molecular dynamics (MD) simulations.
Significant Findings: The IL-functionalized filler enhanced interfacial adhesion, as evidenced by increased thermal stability with delayed degradation and improved glass transition temperature (T_g) from 181.5 to 189.46 °C, reflecting stronger polymer-filler interactions. At 10 wt.% IL-Si, the membrane achieved a CO_2 permeability of 25 Barrer and CO_2/CH_4 selectivity of 37, representing 246% and 208% improvements over neat polysulfone (PSF). Compared to non-modified silica/PSF, the permeability and selectivity improved by 140% and 40%, respectively. MD simulations, with <10% deviation, confirmed $[Tf_2N]^-$ anions enhance CO_2 sorption while $[EMIM]^+$ cations strengthen filler dispersion and compatibility. Based on this, future work needs to focus on testing functionalized ILs, scaling up fabrication, assessing long-term stability under harsh conditions, and expanding membrane studies to other relevant gas pairs.

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1. Introduction

The growing demand for clean energy and the need to mitigate greenhouse gas emissions have intensified research into efficient CO_2 capture technologies. Natural gas, a key transitional energy source, often contains substantial CO_2 that must be removed to improve fuel quality, reduce environmental impact, and prevent pipeline corrosion [1]. In this context, MMMs have attracted considerable attention due to their sustainable and operationally simple nature, as well as their ability to combine the high separation efficiency of inorganic fillers with the mechanical robustness and processability of polymer matrices [2].

In MMMs, the PSF [3,4], a thermally and chemically stable polymer with high gas permeance, has been extensively used as a base material with different inorganic fillers [5,6]. Ramezani et al. [7] studied the incorporation of 20 wt.% ZIF-8 into a PSF matrix enhanced the gas separation performance of the membrane. the CO_2 permeability increased from 76.72 GPU for the pristine PSF membrane to 322.95 GPU for the MMM, and the CO_2/CH_4 selectivity improved substantially from 2.46 to 5.27. The improvement highlighted the potential of ZIF-8 as a filler for enhancing the separation capabilities of MMMs. Pinnau et al. [8] stated that incorporating nonporous, nanosized fumed silica into glassy polymers with high free volume can alter the packing of polymer chains. This alteration increases the available free volume, leading to a notable enhancement in gas permeability. Building on this concept, Hassanajili et al. [9] investigated the effect of silica nanoparticles on the gas separation performance of silica/polyurethane (PU) MMMs. The study revealed that the inclusion of silica disrupted the polymer chain packing, increasing the dynamic free volume and improving gas transport properties. At an optimal loading of 15 wt.%, the silica/PU MMM demonstrated a significant increase in CO_2 permeability, reaching 12.03 Barrer, which represents a 418.5% rise compared to pure PU, along with a CO_2/CH_4 selectivity of 19.26, indicating a 131% enhancement.

Despite these advancements, challenges such as filler agglomeration, poor interfacial compatibility, and limited tunability of gas transport pathways persist, often hindering the overall performance of MMMs [10]. Mohamad et al. [11] developed MMMs by incorporating zeolite-T particles at varying loadings (0.5–5 wt.%) into a PSF matrix. They reported that membranes with 5 wt.% zeolite-T exhibited CO_2 permeability of 66.80 GPU, approximately 441% higher than the pristine PSF membrane. However, the CO_2/CH_4 selectivity decreased to 1.41, which is 47% lower than that of the pristine PSF membrane. These findings demonstrate a trade-off between selectivity and permeability in PSF-based MMMs due to particle aggregation. Ahn et al. [12] examined the effects of silica incorporation into PSF membranes and found that adding 0–20 vol.% silica increased the membrane's free volume compared to the unmodified PSF. This increase, caused by less efficient packing of polymer chains, enhanced both diffusion and solubility coefficients, resulting in improved permeability. For instance, the CO_2 permeability in a membrane with 20 vol.% silica was approximately 213% higher than that of pure PSF. However, a 53% decrease in CO_2/CH_4 selectivity was observed, likely due to the aggregation of silica particles at higher concentrations within the PSF matrix. To address this limitation, IL modifications are particularly notable for their strong affinity for CO_2 and adjustable properties [13]. Numerous studies over the past decade have already explored hybrid systems incorporating imidazolium-based ionic liquids, silica fillers, and polysulfone or other glassy polymer matrices, demonstrating the potential of IL-assisted MMMs for CO_2 separation [14–16]. For example, Shafie et al. [14] developed silica/polycarbonate MMMs blended with [EMIM][Tf₂N], reporting a 13-fold increase in CO_2 permeability and improved CO_2/CH_4 selectivity due to enhanced interfacial interaction and chain mobility. Similarly, Ahmad et al. [16] post-modified PSF/SAPO-34 MMMs with imidazolium-based ILs, achieving over 700% enhancement in CO_2/N_2 selectivity. Cardoso et al. [15] incorporated [EMIM][Tf₂N] in PES/SAPO-34 MMMs and observed better filler dispersion and flexibility at optimal IL loadings. Supported IL membranes (SILMs) using γ-Al_2O_3 or zeolitic supports have also demonstrated high selectivity, though long-term stability remains a limitation due to IL leaching and capillary instability. Similarly, Mustafa et al. [17] fabricated ionic liquid-based MMMs via an impregnation method using 6 wt.% TiO_2 and varying loadings (5–25 wt.%) of the IL [EMIM][DCA]. The ILMMMs exhibited significant permeability enhancements, with 12.7, 17.0, 23.2, and 29.4-fold increases at 5–20 wt.% IL loading, respectively, compared to the corresponding MMM. Selectivity improvements of 1.89, 2.26, 2.67, and 3.01-fold were also observed over the same IL loading range. Despite these performance gains, membrane stability was adversely affected, as evidenced by a reduction in glass transition temperature from 200 to 137 °C with increasing IL content. This trade-off highlights the need to develop membrane systems that achieve enhanced gas separation performance while maintaining adequate thermal and mechanical stability. Nonetheless, identifying suitable fillers, polymers, and ILs requires many trials, as the process involves testing for compatibility and filler propagation. Additionally, measuring membrane morphology and performance in situ is challenging, making experimental testing costly, labour-intensive, and time-consuming.

In this context, computational chemistry has grown as an effective tool that provides fast, atomistic-level elucidation of material properties in the creation and analysis of membranes. It offers a modelling and simulation environment that can be used to anticipate and understand the connections between the molecular structure of a material and its properties, while circumventing the difficulties, costs, or time associated with lab-scale manufacturing [18]. Several computational studies have been conducted on polymers and MMMs [19,20]. For example, Jawalkar et al. [21] employed atomistic and mesoscopic simulations to calculate the Flory-Huggins interaction parameter of poly (N-vinylpyrrolidone)/poly(bisphenol-A-ether sulfone) (PVP/ PES) blends, predicting poor miscibility ($\chi \approx 1.9$), which agreed with the experimentally observed phase separation. In another study, Raghu et al. [22] combined synthesis and MD simulations of novel polyurethanes with different diisocyanates and showed how simulated cohesive energy density, hydrogen bonding and surface free energy correlated with Tg and contact angle measurements. These studies demonstrate that MD can accurately predict the compatibility, interfacial interactions, and surface properties of complex polymer systems before synthesis, providing a powerful complement to experimental membrane development. Khadija et al. [23] further conducted a molecular simulation study on CO_2/CH_4 separation in silica/PSF-based MMM. They varied silica filler loadings (15, 20, 25, and 30 wt.%) to observe their effect on the gas transport properties of MMM. They found that permeability and selectivity consistently increased with the incorporation of silica in the PSF membrane until 25 wt.%, after which they further decreased for 30 wt.%. Karim et al. [24] conducted a simulation study on silica/PSF-based mixed matrix membrane under pure gas conditions, which included O_2, N_2, CO_2, and CH_4 and observed that for 20 wt.% silica, the CO_2 permeability was recorded at 22.5 barrer, representing a 470% increase compared to pristine PSF (3.95 barrer). The simulated results were in close agreement with the experimental values. Hence, it can be concluded that a suitable computational model accurately predicts the separation capability of existing membranes and can subsequently be employed for next-generation membranes used in macroscopic process simulations.

In summary, numerous studies have investigated hybrid membranes that combine ILs, silica fillers, and glassy polymers for CO_2/CH_4 separation. However, most of these studies relied on porous or sol-gel-derived silica, zeolitic fillers, or porous supports, which can lead to polymer penetration into the pores, causing partial pore blockage and reducing the accessible surface area for gas diffusion. Furthermore, most approaches used physical blending or impregnation, which often resulted in pore blockage, IL leaching, and unstable interfaces, thereby limiting long-term performance of membrane. Recently, grafting ILs onto inorganic fillers has emerged as a more robust method to improve polymer-filler compatibility, CO_2 affinity, and structural stability while