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Review

A critical review on advancements and challenges in CO_2 gas separation via 6FDA-based membranes

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ABSTRACT

Membrane technology is at the cutting edge of gas separation, offering energy-efficient and scalable solutions across industries. This review analyses 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)-based polyimides, emphasising their vital role in CO_2 gas separation. It discusses recent advancements and highlights their characteristics: high free volume, thermal stability, and chemical resistance, making them ideal for efficient gas separation. The review also covers fabrication methods for 6FDA-derived membranes, including composite and hybrid types with superior performance. It further examines recent advancements in 6FDA-based polymeric membranes, particularly mixed matrix membranes (MMMs) and hybrid architectures, with a focused discussion on polymer modifications such as thermal rearrangement and cross-linking, as well as the strategic integration of advanced fillers, including metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and ionic liquids (ILs). These advancements collectively contribute to enhanced membrane performance and expand their potential applications in gas separation technologies. For instance, adding 20 wt. % ZIF-67 to 6FDA-Durene significantly increased CO_2 permeability from 669.12 to 1529.86 Barrer. However, this enhancement came at the cost of a slight decrease in CO_2/N_2 and CO_2/CH_4 selectivities. In contrast, incorporating 20 wt. % [Emim][Tf_2N]@ZIF-67 improved CO_2 permeability by 33 %, while also increasing CO_2/N_2 selectivity from 25 to 28 and CO_2/CH_4 selectivity from 24 to 28. This highlights the superior performance of hybrid membranes over other composite formulations. The review highlights molecular simulations' critical role in revealing atomistic interactions and optimising filler-polymer interfaces, addressing scalability issues in experimental separations. These simulations provide insights for developing high-performance membranes. It also offers a comprehensive overview of current research and future directions by discussing experimental findings and molecular dynamics simulations. Additionally, it emphasises the potential of 6FDA-based membranes for industrial applications, indicating that advancements in filler modification and polymer design could help overcome existing challenges.

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1. Introduction

Membranes have emerged as a widely utilized technology for gas separation (Song et al., 2024). These advantages include their environmentally friendly nature, ease of operation, low operational costs, and high efficiency (Safikhani et al., 2021; He et al., 2022). In essence, membranes operate by selectively permitting certain species to pass through while restricting others, thus enabling the efficient separation of gas mixtures. This selective permeability, along with the advantages of membrane technology such as energy efficiency, ease of operation, and scalability, makes it a highly favored method for gas separation (Warsinger et al., 2018; Sanders et al., 2013).

Membranes used in various gas separation applications are mostly fabricated from synthetic polymers, such as polysulfone (PSF), polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), polyethersulfone (PES), polyvinyl alcohol (PVA), cellulose acetate (CA), chitosan (CS), alginates, and polyimides (PIs) (Matabola et al., 2009; Prasad et al., 2018; Wijmans and Baker, 1995; Vatanpour et al., 2022; Bashir et al., 2024; Teh and Yong, 2024). PIs are regarded as the most versatile and high-performance materials for membrane gas separation due to their superior thermal, chemical, and mechanical stability with exceptional gas separation performance compared to other polymer classes. PI polymers specially synthesised using 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) as a monomer (6FDA-based polymer) perform superior gas separation performance (O'Harra et al., 2019; Geng et al., 2024; G Chen et al., 2024). Though 6FDA-based polymers possess a unique combination of properties and applications in various fields (Carpintero-Santamaría and Velarde, 2014; Reinders, 2021; Tchangai et al., 1989; Tsai et al., 2003), their most significant impact is observed in gas separation technologies. 6FDA-based polymers are highly valued for their unique properties in gas separation applications. Flexible substituent groups in their backbone structure contribute to better processability, while bulky and polar groups (CF_3) optimize the balance between permeability and selectivity (Gutiérrez-Hernández et al., 2024; Xu et al., 2020; Lee et al., 2021). These structural features increase inter-chain packing density and expand free-volume, boosting the thermal and mechanical stability of the membranes in demanding environments. With high permeability and selectivity for critical gas pairs such as CO_2/CH_4, H_2/CH_4, and O_2/N_2, 6FDA-based PIs are widely used in natural gas processing, carbon capture, and hydrogen purification. Additionally, these membranes offer strong resistance to plasticisation under high-pressure conditions, a common challenge in gas separation, making them particularly suitable for robust industrial applications (López-Badillo et al., 2019; P Li et al., 2024).

Various 6FDA-based polymers (as shown in Table 1) are specifically tailored for their diverse gas separation applications, leveraging their unique structural and physical properties. For instance, 6FDA-DAM exhibits excellent separation performance due to its high free volume, making it suitable for challenging gas combinations, such as CO_2/CH_4, where both permeability and selectivity are critical (Park et al., 2014; Park et al., 2024). Likewise, 6FDA-ODA (oxydianiline) balances permeability and mechanical robustness, enabling its use in high-pressure scenarios. These materials are also effective for separating other gas pairs, such as CO_2/O_2 and CO_2/N_2, due to their customizable chain structures and intrinsic molecular transport properties (M.Z. MZ Ahmad et al., 2018). By fine-tuning the polymer composition, free volume, and chain rigidity, 6FDA-based membranes can meet the separation requirements of various industrial gases, thereby ensuring high performance and stability (López-Badillo et al., 2019; Roy et al., 2020; M.Z. MZ Ahmad et al., 2018; Qiu et al., 2014; Jeon et al., 2020).

Blended membranes such as 6FDA-polyetherimides, MMMs with inorganic fillers, and 6FDA cross-linked systems further broaden the application spectrum of 6FDA-based materials, enhancing their stability and performance (M.Z. MZ Ahmad et al., 2018; Nik et al., 2012; Shirvani et al., 2019; Neyertz et al., 2023; Yerzhankyzy et al., 2022).

However, despite the advantages of 6FDA, challenges remain in optimizing the performance of 6FDA-based membranes. Issues such as aging, plasticisation under high pressures, and trade-offs between permeability and selectivity still need to be addressed (Jheng et al., 2023; X Zhou et al., 2023). The gas separation performance of polymeric membranes is directly correlated with their chemical composition and physical structure (Zhao et al., 2023; Jana and Modi, 2024). As a result, the investigation into the structures and characteristics of polymers is of significant interest and a persistent challenge in the advancement of membranes (Rong et al., 2001; Kansara et al., 2019; Pan et al., 2007). Emerging research trends focus on integrating advanced fillers like ILs, MOFs, and ZIFs into 6FDA-based MMMs, which enhance both gas separation performance and the durability of membranes (Selvaraj and Wilfred, 2024; Y Liu et al., 2018; Shafiq et al., 2021). Additionally, surface modifications and the development of cross-linked networks and carbon molecular sieves (CMS) are being explored to improve membrane stability and reduce aging effects, driving advancements in the field (Dai et al., 2017; D.Q. DQ Vu et al., 2003).

While there are numerous exemplary evaluations concerning membrane-based gas separation, a comprehensive review concerning using 6FDA-based polymeric, blended, MMM and its hybrid membranes for gas separation is still lacking. Favvas et al. (2017) provided a detailed review of PI membranes for CO_2 separation, emphasising the role of fundamental mass transfer phenomena in determining separation efficiency. Baig et al. (2021) highlighted the versatility of PI membranes, particularly their super-wettability for oil-water separation, focusing on surface engineering to enhance separation performance. Y Li et al. (2022) explored advancements in low-dielectric PI films, shedding light on structural modifications to improve thermal and chemical stability. However, to our knowledge, no review has comprehensively examined the gas transport mechanisms, performance optimisation strategies, and recent advancements, specifically in 6FDA-based PI membranes. Additionally, a thorough examination of the structure-property relationships of 6FDA-based PIs for producing high-performance membranes needs to be explored (Huang et al., 2023; Z. Z Liu et al., 2020; Yang et al., 2024).

In this study, a distinct focus is placed on the challenges associated with experimental scale separation, emphasising the need for cost-effective and time-efficient alternatives. This shifts towards the Molecular Dynamics (MD) simulation approach, a powerful tool capable of elucidating physical properties, morphological alterations, and gas transport behaviour at the molecular level (Balçık et al., 2021; J Liu et al., 2023; Hira et al., 2023). The findings underscore the development in enhancing gas separation performance and highlight the lasting challenges that necessitate a joint approach combining experimental insights and computational simulations. This review seeks to address this gap by providing an in-depth analysis of the synthesis, structural properties, and gas separation performance of 6FDA-based membranes. It also considers molecular simulation studies that offer molecular insights into their gas transport mechanisms.

The review commences with an introduction that emphasises the importance of membrane technology in gas separation and highlights the distinctive characteristics of 6FDA-based materials. It then explores various synthesis techniques, including pure polymeric, blended, composite and hybrid membranes. Next, the performance of 6FDA-based polymeric and MMMs that integrate advanced fillers, such as MOFs, ZIFs, and ILs, in CO_2 gas separation is assessed, focusing on their permeability and selectivity across different gases. Additionally, the review investigates the significance of molecular simulation studies, demonstrating how these simulations can forecast gas transport dynamics and enhance membrane performance. It also discusses current challenges and limitations, including scalability and the inherent trade-offs between permeability and selectivity in 6FDA-based polymeric, mixed and hybrid membranes. The review concludes by suggesting future research directions to push the boundaries of 6FDA-based PIs that could lead to innovative advancements in this field.