

Design Strategies for Enhancing Gas Separation with High-Performance Mixed Matrix Membranes

Mehdi Ghasemi*, Lev Sarkisov, Masoud Babaei

Department of Chemical Engineering, The University of Manchester, Manchester, M13 9PL, UK

Abstract

In response to the imperative for developing efficient techniques to capture carbon dioxide (CO₂) from industrial processes, membrane-based gas separation holds significant promise for its cost-effectiveness, safety, environmental benefits, and energy efficiency.¹ Among the wide variety of materials applicable to this technique, polymeric materials have predominantly captured attention for their suitability for large-scale deployment.² Despite the successful commercialization of polymeric membranes, they suffer from the permeability-selectivity trade-off.³ A promising approach to address this issue involves the utilization of mixed matrix membranes (MMMs), formed by integrating porous materials as fillers into a polymer matrix.⁴ MMMs leverage the processability of polymeric membranes along with the superior selectivity and permeability of porous materials. In the development of efficient MMMs, several critical factors come into play, including the morphologies of MMMs, types of polymers, filler particle types, particle dispersion, plasticization, and physical aging.⁵ Enhancing MMM performance is also achievable through modifications, such as adjusting filler size, shape, and loading, adding additives, and implementing filler surface modifications.⁶ This research focuses on how geometrically optimized fillers can improve the efficiency of designed MMMs for gas separation.

The first step toward an efficient design strategy for ideal MMMs is to determine the most perm-selective polymer-filler combination. Most theoretical macroscopic predictive models developed for MMMs (Maxwell model⁷ and Lewis and Nielsen⁸ model) are based on an analogy between fluid permeability in heterogeneous membranes and thermal or electrical conductivity in composite media. However, these models are typically limited to studying the transport of a single gas in idealized systems with spherical filler particles and fail to capture the complexities of experimentally fabricated membranes. To overcome these limitations, particularly in accounting for the impact of geometrical features on the effective transport properties of MMMs, 3D numerical-based approaches offer a promising alternative.

In the first part of the study, a computational approach using a voxel-based finite element method (FEM) was developed for a systematic investigation of how Platonic-shaped fillers influence the criteria for designing optimal membranes. The assessment of single-gas transport in MMMs with randomly distributed fillers revealed that filler particles with varying sphericity—but identical volume—can significantly impact the effective permeability of MMMs (Fig. 1). A reduction in filler sphericity, such as in tetrahedral structures compared to spherical ones, leads to a substantial

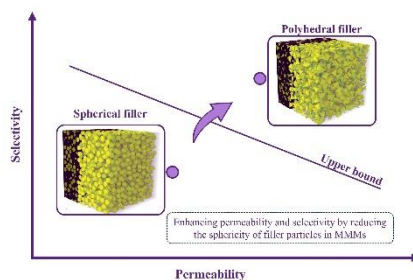


Fig. 1. Impact of filler shape on the performance of MMMs in surpassing the upper bound limit

enhancement in effective permeability, primarily due to the formation of more interconnected pathways. This effect becomes increasingly pronounced at higher filler loading fractions and filler-to-polymer ratios. Furthermore, binary gas transport assessments demonstrated that filler particle shape plays a crucial role in determining the optimal filler-matrix combination, particularly regarding phase gas transport compatibility for maximizing selectivity in gas mixtures. Filler particles with lower sphericity achieve higher maximum selectivity; however, this occurs alongside a partially higher filler-to-polymer permeability for faster gas flow compared to spherical fillers (Fig. 2).

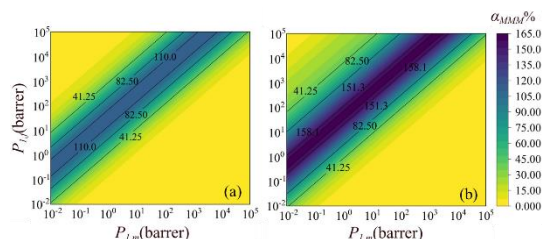


Fig. 2. Colour maps indicating the percentage increase in selectivity for a wide range of perm-ratios of the faster gas for (a) spherical fillers and (b) tetrahedral fillers.

The second step in the design of MMMs involves determining the origins of incompatibility when ideal MMMs are not achieved and developing strategies to overcome these challenges effectively. Over the past decade, considerable efforts have been devoted to producing defect-free MMMs. This, however, proved to be challenging as the structure of the final membrane strongly depends on the compatibility (or in other words, interaction) between the filler surface and the polymer chains. In general, we define a defect as a region around the filler particle, with unique properties different from both the filler and polymer matrix materials. Depending on the nature of interaction between the filler surface and polymer chains, in this region, polymer chains undergo rigidification or dilution.⁹ The former arrangement causes the blockage of pores within the porous fillers, resulting in varying reductions in permeability (or increases in selectivity), depending on the degree of blockage, compared to the polymer bulk. Conversely, the dilution results in the creation of nonselective voids around filler particles, leading to increased permeability (or decreased selectivity) relative to the polymer matrix.⁵ In general, presence of defects in a non-ideal membrane may lead to the deterioration of the MMMs in a separation process.¹⁰ However, even more importantly, presence of defects makes it difficult to predict properties of the MMMs using classical transport theories. The ability to detect defects in MMMs and predict their impact on transport properties is essential for the development and implementation of MMM-based technologies.

Using the previously developed computational model in application to CO₂ separation as a case study, we explore the intricate relationship between the geometrical features of interfacial defects, the arrangements of filler particles and the emerging transport pathways. We show that the perm-selectivity is directly influenced by the geometry of interfacial defects and filler particles, the configuration of defect regions, the spatial distribution of filler particles, and the gas permeability in each phase (Fig. 3). Our findings indicate the arrangement of filler particles, and the overlap of defect regions are two key sources of uncertainty in predicting membrane permeability and selectivity. Filler particles positioned on the membrane surface, particularly when connected defect regions are present, can either increase or decrease perm-selectivity depending on whether the defects are voids or rigidified polymers, relative to macroscopic predictive models. In contrast, uniformly distributed filler particles with no overlapping defect regions show results that closely align with theoretical model predictions. In addition, the impact of interfacial thickness and filler volume fraction on membrane performance should be evaluated with consideration of filler shape. While non-ideal characteristics may compromise ideal perm-selectivity, polyhedral filler structures, sharing similar defect characteristics with the filler particles, exhibit higher perm-selectivity compared to spherical fillers with spherical defect shapes under identical conditions. Moreover, the greater the deviation of the defect structure from a spherical shape toward one with lower sphericity, the higher the perm-selectivity observed. These enhanced performances are primarily attributed to the increased potential of polyhedral defect structures to create interconnected pathways. These findings offer valuable insights for the strategic enhancement of permeability and selectivity in MMMs through the integration of structurally diverse porous materials and for the detailed characterization of interfacial defects, which are crucial for optimizing the performance of MMMs.

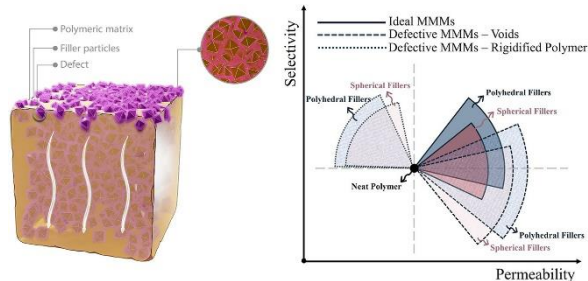


Fig. 3. (a) Illustration of MMMs showing particles distributed on the membrane with overlapping defect regions. (b) Impact of variations in filler particle geometry and defect interphase on perm-selectivity

Keywords: Gas separation; Mixed matrix membrane; Perm-selectivity; Design strategy; Membrane simulation

References: ¹Baker, R.W., 2002. Future directions of membrane gas separation technology. *Industrial & engineering chemistry research*, 41(6), pp.1393-1411. ²Koros, W.J. and Mahajan, R., 2000. Pushing the limits on possibilities for large scale gas separation: which strategies?. *Journal of Membrane Science*, 175(2), pp.181-196. ³Robeson, L.M., 1991. Correlation of separation factor versus permeability for polymeric membranes. *Journal of membrane science*, 62(2), pp.165-185. ⁴Dong, G., Li, H. and Chen, V., 2013. Challenges and opportunities for mixed-matrix membranes for gas separation. *Journal of Materials Chemistry A*, 1(15), pp.4610-4630. ⁵Vinh-Thang, H. and Kaliaguine, S., 2013. Predictive models for mixed-matrix membrane performance: a review. *Chemical reviews*, 113(7), pp.4980-5028. ⁶Kamble, A.R., Patel, C.M. and Murthy, Z.V.P., 2021. A review on the recent advances in mixed matrix membranes for gas separation processes. *Renewable and Sustainable Energy Reviews*, 145, p.111062. ⁷Maxwell, J.C., 1873. *A treatise on electricity and magnetism* (Vol. 1). Clarendon press. ⁸Lewis, T.B. and Nielsen, L.E., 1970. Dynamic mechanical properties of particulate-filled composites. *Journal of applied polymer science*, 14(6), pp.1449-1471. ⁹Niu, Z., He, N., Yao, Y., Ma, A., Zhang, E., Cheng, L., Li, Y. and Lu, X., 2024. Mixed matrix membranes for gas separations: a review. *Chemical Engineering Journal*, p.152912. ¹⁰Lin, Z., Yuan, Z., Dai, Z., Shao, L., Eisen, M.S. and He, X., 2023. A review from material functionalization to process feasibility on advanced mixed matrix membranes for gas separations. *Chemical Engineering Journal*, 475, p.146075.
