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Computer-Aided Design and Fabrication of Advanced Membranes for Nitrogen/Methane Separation

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Abstract. One of the effective strategies for advancing the goals of process intensification is the purposeful introduction of reproducible structures through a combination of computer-aided molecular design and print-assisted fabrication techniques. In this study, molecular models of two polymers—MDA and ODA—were developed using Avogadro software. These models were subsequently fabricated into membranes using a print-assisted method, specifically employing a LaserJet printer to produce structured flat-sheet composite membranes. The membranes were evaluated for their performance in N_2/CH_4 gas separation. Characterization of the membranes was conducted using microscopy, while gas transport properties and separation performance were assessed via constant-pressure gas permeation tests, measuring both permeability and hydraulic resistance. Although the same substrate was used for printing both polymers, the hydraulic resistance varied significantly between the materials and the gases tested. For MDA, resistance to N_2 and CH_4 ranged from 38,560.78 to 95,697.10 kPa·s/m³, whereas ODA exhibited a range of 28,132.33 to 88,124.16 kPa·s/m³. In terms of selectivity for N_2/CH_4, ODA demonstrated values of 2.34 and 3.10 for single-layer and seven-layer membranes, respectively, compared to 1.71 and 1.92 for MDA under the same conditions. Morphological analysis revealed that the printed membranes possessed well-defined structures with evenly distributed voids, contributing to enhanced reproducibility and predictability in performance. Overall, the fabricated membranes exhibit promising characteristics for intensifying membrane-based separation processes, particularly in the context of N_2/CH_4 separation.

Introduction

The demand for engineered membrane materials has risen rapidly owing to a drastic increase in the demand for membrane separation equipment and processes for gas separation. The growing interest in the industrial application of membrane technology is due to its intrinsic beneficial features, such as high energy efficiency, operation simplicity, modularity, lower footprint, no phase change involved, low weight, low maintenance, and ease of scaling up [1]. Despite some initial successes in various membrane materials fabrication methods, many challenges remain in developing membrane materials that are suitable for separating a variety of gas mixtures. The performance of a membrane separation system is dictated by the semi-permeable membrane materials employed for the separation. In most cases, the materials are made with polymers with known chemical structures. Therefore, majority believe that molecular design and engineering methods that allow the tailoring of the physical, chemical and micro-structural properties of

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polymers is the most successful method to enhance the separation performance [2]. Much research effort has been published on chemical modifications of polymers which resulted in controlling the gas separation performance of the membrane [3,4,5,6,7,8]. The practice of chemical modification of polymer followed by subsequent synthesis and fabrication of these membranes involves series of chemical processes and the use of hazardous volatile solvents and chemicals which are dangerous to both researchers and the environment at large. In addition, the processes are also time-consuming and may involve the use of expensive chemicals and reagents. It is therefore imperative to devise a means of simulating the performance of these polymers as membranes before fabrication. The simulation can be used as a quick screening tool to reduce waste, cost and time, save the environment and safeguard the health and safety of researchers. A computer-aided molecular design and print-assisted fabrication is thereby proposed as a tool for the design and fabrication of membranes for gas separation.

In this study, the incorporation of the inkjet coating procedure into the membrane fabrication process was demonstrated using a complex mixture of nanoparticles, polymers and dyes. The capabilities of the produced membranes for the separation of various gas mixtures were investigated. The application of inkjet printing in membrane fabrication could facilitate the production of mixed-matrix membranes with uniformly distributed nanoparticles. Thus, the central aim of this study is to evaluate the fundamental physio-chemical properties of a membrane that is designed by molecular design software and then fabricated using inkjet printing as a deposition and patterning tool. Specifically, molecular design of MDA and ODA was carried out using Avogadro software. The designed polymer was then printed using an inkjet printer. The printed membrane was evaluated in terms of the gas permeability and selectivity of the membrane.

It is expected that this work will open a new frontier in the approach used for membrane design and fabrication. It will also provide some insights into how membrane performance can be simulated and predicted before carrying out the practical routes of its synthesis in the lab. Membranes produced with this type of method are expected to possess a uniform and repeatable morphology, which will make it easier to understand the membrane physico-chemical behaviours and predict their performance. The understanding of the physio-chemical behaviours can ultimately provide insight required for accurate prediction of membrane performance.

Methodology and Materials

The materials used in this research include an inkjet printer, ink, lignocellulosic paper-based gases (CH_4 and N_2). Molecular design of two polymers, 4,4'-Oxydianiline (ODA) and methylenedianiline (MDA) was done using Avogadro's software. The optimized geometry was then duplicated to many molecular chains. The chains were arranged side by side. The two polymers were then printed using ink-jet printer [9,10,11,12]. The flat sheet membrane was printed using word processing software and a laser jet printer.

The morphology of the fabricated membrane samples was studied using SEM and Digital Microscope USB X1000 RoHS to capture an optical image of the sample surfaces and cross-section.

Hydraulic resistance and gas permeability were measured by a constant pressure/variable volume apparatus. Detailed information about this apparatus has been published elsewhere [13]. The apparatus is composed of the permeation cell and a gas flowmeter on the downstream side. At steady-state condition, gas permeability was calculated using,

$$P = \frac{22.414}{A} \frac{l}{(p_2 - p_1)} \frac{p_1}{RT} \frac{dV}{dt} \quad (1)$$

where A is the membrane area (cm^2), p_2 and p_1 are feed or upstream and permeate or downstream pressures, respectively, R is the universal gas constant (6236.56 cm^3 cm Hg/mol.K), T is the

absolute temperature (K), *dV/dt* is the volumetric flow rate obtained from the flowmeter (cm^3/s) and 22.414 is the number of cm^3 STP of penetrant per mole [14,15].

Results and Discussion

Figs. 1 and 2 provide information about the uniformity of deposition and dispersion of particles in the substrate. Fig. 1(a) shows a clear distinction between the deposited layer and the underlying substrate, with the former being a black layer overlaying the whitish cellulosic paper support. This optical comparison validates the effective formation of the layers through the LaserJet printing-assisted method. Fig. 1(b)-(f) shows the structural development in terms of more layers. As an example, the distribution of the active phase in Fig. 1(e) of the single-layer printed membrane is relatively homogeneous, similar to that of the seven-layer samples. The uniformity of the microstructural arrangement of different thicknesses indicates that the print-assisted fabrication method can support the formation of mixed-matrix membranes with dispersed phases across the entire continuous matrix.

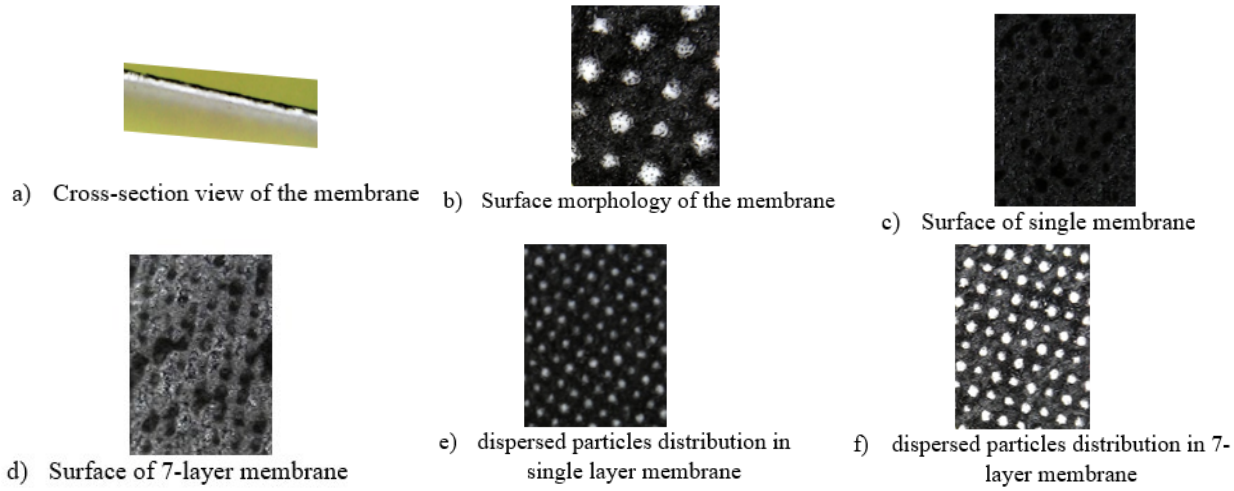
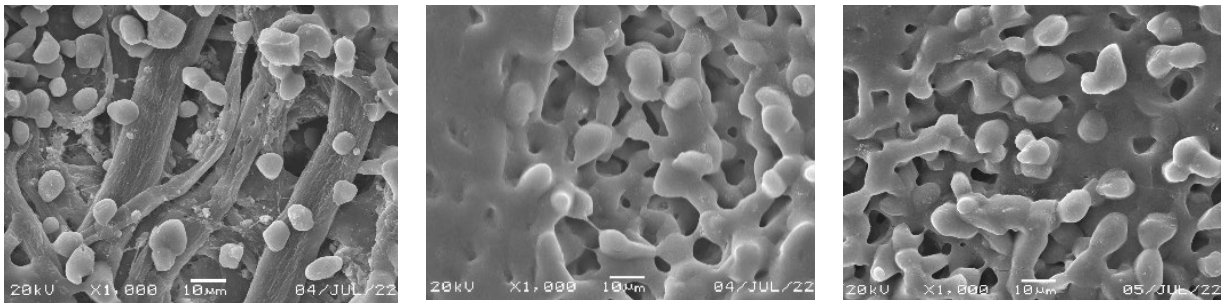


Figure 1 *Optical microscopic images of different layers of printed membranes.*



(a) Particles in single-layer (b) Particles 3-layer (c) Particles in 7-layer

Figure 2 *SEM images of membrane samples for different layers of printed membranes.*

Optical microscopy observations (Fig. 1) are also supported by SEM analysis (Fig. 2), which gives evidence of the microstructural features at a higher resolution. SEM images show that the particles of ink are not only deposited on the surface but also embedded into the fibrous structure of the cellulosic substrate and create a cohesive interface between the active and support layers. Additionally, the lack of large agglomeration or void formation at the interface indicates a stable fabrication process that can be used to generate defect-reduced mixed-matrix membranes that can be used in gas separation.

Gas transport properties

As shown in Table 1, the hydraulic resistance measurements are in close agreement with what was seen in the SEM images. Both MDA and ODA single-layer membranes exhibited a high number of very fine pores, but the ones in ODA were slightly bigger, albeit by a very small margin. This slight variation assisted in lowering the flow resistance, particularly in the case of methane (CH_4). As an example, the CH_4 resistance of the single-layer ODA membrane was approximately 28,132 kPa s/m³, which was significantly lower than that of MDA, 38,561 kPa s/m³. In the case of nitrogen (N_2), the two membranes showed nearly identical resistance (65,827 and 65,933 kPa s/m³ for MDA and ODA, respectively), indicating that the slight difference in pore size between the two polymers was not significant to this gas. Though the exact reason for this behaviour needs to be further investigated, N_2 is known to be less condensable and has weaker interactions with the polymer matrix and is more dependent on overall pore connectivity rather than small changes in pore size. At a membrane thickness of seven layers, the SEM images revealed that the surfaces became rougher and some of the pore mouths were partially blocked or misaligned between layers. This stratification effect automatically increased resistance to gas flow, since gases had to travel through more interfaces and through a more tortuous path. In the case of MDA, there was a definite rise in resistance to both gases: CH_4 to approximately 49,868 kPa s/m³ and N_2 to 95,697 kPa s/m³. The greater rise in N_2 indicates that the added roughness and narrower passages in the layered structure were more difficult for the smaller gas to flow through.

Table 1 *Hydraulic Resistance of Various Layer Membranes*

Polymer	Layer	Gas	Hydraulic resistance
MDA-1-layer	Single	N_2	65826.79
ODA-1-layer	Single	N_2	65933.37
MDA-7-layer	7-layer	N_2	95697.10
ODA7-layer	7-layer	N2	88124.16
MDA-1-layer	Single	CH_4	38560.78
ODA-1-layer	Single	CH_4	28132.33
MDA-7-layer	7-layer	CH_4	49867.72
ODA-7-layer	7-layer	CH_4	28425.523

In the case of ODA, the resistance of N_2 increased significantly (from about 65,933 to 88,124 kPa s/m³) when more layers were added, but the resistance of CH_4 remained very small (28,132 to 28,426 kPa s/m³). This indicates that the slightly larger pores and improved orientation of layers in ODA allowed the preservation of open CH_4 pathways, even after stacking. The ODA layered structure thus dealt with the increased complexity more effectively than MDA, probably because the pores were more continuous throughout the stack and less likely to be choked off at the interfaces. Comparing the two polymers, the findings indicate that although both MDA and ODA single-layer membranes have similar performance with N_2, ODA has a lower resistance to CH_4 and keeps it after layering. However, DA is penalized more when stacked, especially on N_2. This is the direct translation of what is observed in the SEM: MDA-stacked membranes appear rougher and more blocked on the surface, whereas ODA are more open and better connected.

In summary, the microstructure has a strong effect on the hydraulic resistance trends. Single layers have the advantage of a high density of fine pores, but even a slight difference in pore size can lower resistance to larger, more condensable gases such as CH_4. The more layers added, the more resistance is added in both cases, but the surface roughness and layer alignment are important factors to avoid excessive pressure drops. Of the two, ODA was more stable in structure when layered, whereas MDA was more susceptible to stacking effects.

Permeability and selectivity

The gas permeability measurements of single-layer and septuple-layer membranes produced with MDA and ODA inks indicate a clear change in gas transport behaviour, which is caused by the structural change brought about by the consecutive deposition of the layers and by the nature of the ink-substrate interface. As shown in Fig. 3(a) the permeability of methane decreased to 0.0219 (seven layers) and 0.0257 cm³ (STP) cm/(cm² scmHg) (single layer) in the case of MDA-based membranes, and so did the permeability of nitrogen to 0.0114 and 0.0151 (cm³ (STP) cm/(cm² scmHg). A similar tendency was observed in ODA-based membranes, where the nitrogen permeability decreased to 0.0124 cm³ (STP) cm/(cm² scmHg); interestingly, the permeability of methane slightly increased to 0.0384 with each additional layer.

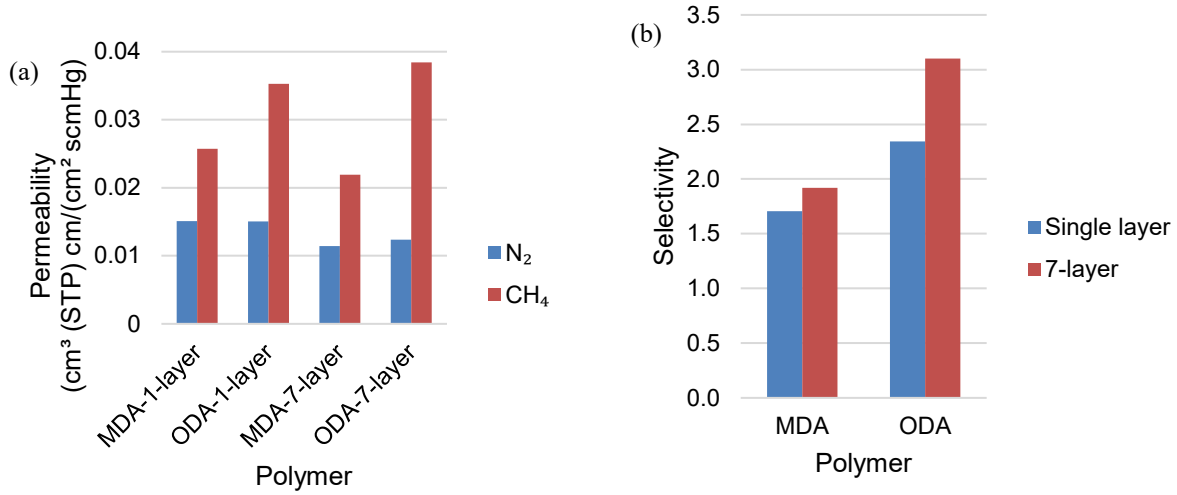


Figure 3 *(a) Nitrogen (N_2) permeability of single-layer and seven-layer MDA and ODA membranes, showing the impact of membrane layering and polymer type on gas transport, and (b) CH_4/N_2 selectivity of single-layer and seven-layer MDA and ODA membranes, illustrating the enhancement in gas separation efficiency upon increasing the number of layers.*

These differences in permeability indicate that there is a layer-dependent modulation of the transportation of gases: MDA membranes are more likely to become densified with extra layers, whereas ODA membranes are more likely to exhibit increased methane permeability, which is likely to be caused by minor changes in the interfacial packing and the mobility of polymer chains. CH_4/N_2 selectivity increased significantly as the number of deposited layers increased in both membrane systems. The selectivity of MDA-based membranes increased by 1.71 (single layer) to 1.92 (seven layers), and ODA-based membranes increased by a more significant margin of 2.34 to 3.10 as in Fig. 3(b). This observation suggests that the extra layers enhance the molecular-sieving effect and probably reduce the occurrence of non-selective defects that would otherwise promote the diffusion of nitrogen. These observations are in line with the data of morphological and structural characterization. SEM micrographs (Figs. 1 and 2) indicate that there is a relatively homogenous distribution of ink particles in the cellulosic matrix, and the seven-layered membranes have a more continuous and compact deposition as compared to the single-layered specimens. This densification effect is probably one of the causes of the reported decrease in gas permeability, especially in the case of the MDA membranes, as it reduces the effective transport pathways and raises tortuosity. The slight rise in CH_4 permeability after multilayer deposition in the case of ODA membranes can be explained by the fact that interfacial compatibility between the ink and substrate was improved due to the more integrated and smooth deposition patterns in the SEM micrographs.

In the case of the ODA membranes, the higher CH_4 permeability of the seven-layer sample can be attributed to the fact that the rigid amorphous fraction was reduced slightly, thus facilitating the

diffusion of CH_4 without significantly reducing N_2 rejection. Generally, the gas permeation properties presented herein demonstrate a subtle interaction between layer thickness, particle distribution, crystallinity and interaction of functional groups. Single-layer membranes had a relatively high permeability, and seven-layered structures provided better selectivity, especially in ODA-based systems. These results demonstrate the urgent need to optimize the number of deposited layers to balance flux and selectivity in specific gas-separation processes.

Conclusion

This study successfully demonstrated the feasibility of print-assisted fabrication of membranes with controlled layer deposition ranging from 0 to 10 layers. Physicochemical characterization results showed a clear difference in both hydraulic and gas separation performance (in terms of permeability and selectivity between N_2 and CH_4), uniform distribution of the particles throughout the layers; and the presence of sulphate, phenolic, and carbohydrate-related functional groups that provided structural framework. The single-layered membranes were expectedly relatively more permeable whereas seven-layered membranes were more selective. These results indicate that print-assisted methods have the potential to produce scalable membranes with reproducible microstructures for gas separation. It can also serve as a tool for predicting the performance of a new polymer for a membrane before synthesis. Further research is needed to investigate more polymer structures and create a database for structure-property relationships for a number of polymers for membrane fabrication. Moreover, the print-assisted method can serve as a strong tool for evaluating the performance of mixed-matrix membranes for gas separation.

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