

Original Research

## Modeling CO<sub>2</sub> and N<sub>2</sub> Permeation through Mixed Matrix Membranes Containing Oxygenated Carbon Nanotubes Dispersed in Polysulfone

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### Abstract

Mixed matrix membranes (MMMs) consist of a polymeric phase and a dispersed solid filler such as zeolites or carbon nanotubes. We prepared symmetric and asymmetric polysulfone-based MMMs containing functionalized multi-walled carbon nanotubes (MWNT-O) for CO<sub>2</sub>/N<sub>2</sub> separation. Maxwell's model was used to predict the permeabilities of MMMs. The permeability achieved using the model exhibited a good fit of the model in symmetric MMMs, especially for CO<sub>2</sub>. This can be potentially attributed to the high affinity of the system toward the polymer matrix. The permeability recorded using Maxwell's model could not reflect the properties of the asymmetric membranes, and this could be attributed to the generation of voids around the fillers or defects present on the surface of the skin. Finally, a mathematical fit was proposed to improve prediction accuracy for both the MMM systems.

### Keywords



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Mixed matrix membranes; functionalized carbon nanotubes; polysulfone; Maxwell's model permeability; permeation

## 1. Introduction

Mixed matrix membranes (MMMs) are one of the most relevant alternatives to ordinary polymeric films that can be used to achieve gas separation. These systems can be potentially used to address the problems of permeability and selectivity tradeoff. It is composed of a solid phase dispersed in a polymer [1]. The high selectivity of the solid filler, attributable to the increase in the number of voids, promotes the permeation of small molecules and improves the permeant sorption selectivity. This property is combined with the high permeability of the polymeric matrix [2] to fabricate the desired materials. Recently, a combination of diffusion and sorption selectivities has been used to fabricate MMMs. Amine-functionalized mesoporous silica that can be used as fillers in MMMs to achieve CO<sub>2</sub> separation has gained importance [1]. Different fillers, such as zeolites and silica, have been investigated [2]. Carbon nanotubes (CNTs) show good permeability as they have extremely smooth walls and contain pores with large diameters. The rate of transport of gas molecules through these pores is higher than the rate of transport recorded for other materials, such as zeolites [3]. However, the extent of dispersion achieved for unmodified CNTs is poor, and these systems usually cluster in polymeric matrices. The formation of the clusters can be attributed to the high aspect ratio (the length to diameter ratio) [4]. If the filler agglomerates, it forms a non-dispersed phase that results in the formation of defects in the membrane. The filler functions as a porous film that is not selective toward any gas. Hence, Wong and coauthors [3] investigated the use of multi-walled carbon nanotubes (MWCNT) functionalized with beta-cyclodextrin as a filler that can be used for the fabrication of polyethylene glycol (PEG)/polyethersulfone (PES) membranes for CO<sub>2</sub>/N<sub>2</sub> separation. The best result was reported when 0.02 wt.% of the filler was used. CO<sub>2</sub> permeance and selectivity against N<sub>2</sub> were recorded to be 12600 GPU and 1.235, respectively.

We investigated the use of multi-walled CNTs functionalized with oxygenated groups (MWNT-O) as fillers for the fabrication of polysulfone membranes [4]. The main goal was to improve the transport properties (flux and selectivity) of MMMs. These properties can be improved by tuning the dispersion and interfacial adhesion properties of the filler. The filler studied by us dispersed well within the polymeric matrix and adhered strongly to the matrix via the oxygenated groups [5]. The use of polysulfone as the polymer was based on the high selectivity of the material for CO<sub>2</sub>/N<sub>2</sub> separation. Polysulfone is a model system that is used for the separation of flue gases [6]. Although polysulfone can be used to achieve good CO<sub>2</sub> separation performance, especially under conditions of low plasticization, the low permeability of such films indicates that the use of asymmetric membranes with a layer of thin skin can be used during separation [7, 8].

We aimed to develop a mathematical model to predict the CO<sub>2</sub> and N<sub>2</sub> permeation behavior of symmetric and asymmetric MWNT-O-containing polysulfone membranes. The model proposed by Maxwell to describe the permeability of gases through MMMs is based on the good dispersion of the fillers [2], and it is noteworthy that achieving a good extent of dispersion is difficult. We also evaluated an empirical model to account for the possible heterogeneities in the composite polymeric membrane [9].

## **2. Materials and Methods**

### **2.1 Materials**

Polysulfone (molar mass: 35000 g/mol), used for the synthesis of polymeric membranes, was obtained from Sigma Aldrich (San Louis, USA). The solvents *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) were obtained from Neon (Suzano, Brazil). N<sub>2</sub> and CO<sub>2</sub> gases (purity: 99.0%) were supplied by White Martins (Contagem, Brazil). The multi-walled CNTs functionalized with oxygenated groups (MWNT-O) were supplied by the CTNano/UFGM Nanomaterials Laboratory (Belo Horizonte, Brazil).

### **2.2 Membrane Synthesis**

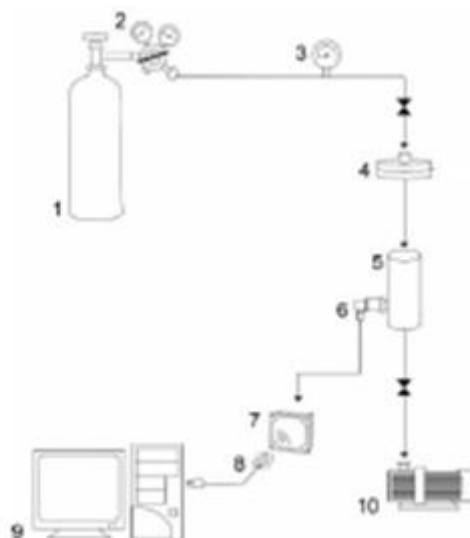
Polysulfone and polysulfone/MWNT-O membranes with two different morphologies (symmetric (dense) and asymmetric (dense skin)) were prepared. The first method was developed to understand the behavior of the MMM system itself, while the second method allows the investigation of the possible increase in flux. The decrease in the membrane thickness (initial thickness: 1 μm) can potentially result in an increase in the flux to 10<sup>4</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup>·s·cmHg.

The symmetric membranes were prepared following the solvent evaporation technique, and the MMMs were prepared with 0.1, 0.5, and 1 wt.% of MWNT-O. The polymer solution used to fabricate the membranes consisted of 15 wt.% of PSF in NMP. The suspension was cast on a plate and placed in an oven heated to 80°C, and the samples were heated for 24 h. The membranes were removed from the plate and stored in a desiccator for future use and characterization.

The asymmetric membranes were prepared following the phase inversion technique. The samples were separated by immersing them in a non-solvent (water). MMMs containing different weight percentages of MWNT-O (1, 3, and 5 wt.%) were used during the fabrication process. The polymer solution used for the fabrication of the membranes consisted of 20 wt.% of PSF in NMP. The suspension was cast on a plate and placed in a water bath for 24 h. The membranes were dried at 25°C for 24 h, and they were subsequently placed in an oven at 80°C for 24 h. The membranes were removed from the plate and stored in a desiccator for characterization.

### **2.3 Permeation Tests**

Gas permeation tests were performed in a standard permeation system that allows the determination of membrane permeability. The method of constant volume and variable permeate pressure was used to arrive at the results. During the execution of the method, the temperature and pressure of the feed gas were kept fixed. The permeate side was characterized by a fixed volume. The experimental setup is shown in Figure 1. Permeability is determined by monitoring the increase in the pressure and the permeate volume as a function of time. The permeability of CO<sub>2</sub> into polysulfone increases with a decrease in the operating pressure. Tests were performed under pressures of 1 and 2 bar at room temperature (25°C).



**Figure 1** Standard gas permeation setup. 1) Gas cylinder; 2) gas valve; 3) manometer; 4) permeation cell; 5) reservoir; 6) pressure transducer; 7) data logger; 8) connecting cable; 9) computer; 10) vacuum pump.

The permeate time and pressure data were plotted following the linear regression method to obtain the slope of the line that represents the gas permeation rate. The permeability (P) was determined from Equation 1, and the permeance (Q) was obtained from Equation 2 [5] as follows:

$$P = \frac{V_s \cdot L}{A \cdot T \cdot p_1} \cdot \frac{T_{STP}}{\rho_{STP}} \cdot \frac{dp_2}{dt}, \tag{1}$$

$$Q = \frac{V_s}{A \cdot T \cdot p_1} \cdot \frac{T_{STP}}{p_{STP}} \cdot \frac{dp_2}{dt}, \tag{2}$$

where A is the effective membrane area (in cm<sup>2</sup>), V<sub>s</sub> denotes the constant volume of the system for reserved permeate gas (in cm<sup>3</sup>), L is the thickness of the membrane (in cm), p<sub>1</sub> and p<sub>2</sub> are the feed and permeate pressures (in bar), respectively, t is the time (in seconds), and T is the temperature (in Kelvin). The STP index represents the standard conditions for temperature and pressure (273.15 K and 76 cmHg, respectively). Gas permeability through a membrane is commonly expressed in the units of Barrer, where 1 Barrer is equal to 10<sup>-10</sup> cm<sup>3</sup> (STP).cm/cm<sup>2</sup>.s.cmHg, and permeance is expressed in the units of Gas Permeation Unit (GPU), where 1 GPU is equal to 10<sup>-6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup>.s.cmHg.

### 2.4 Maxwell Model

Permeability was determined, and the data were fit using the permeability model proposed by Maxwell (Equation 3) to analyze the results. Permeability was determined as follows:

$$P_{MMM} = P_C \frac{P_D + 2P_C - 2\phi_d(P_C - P_D)}{P_D + 2P_C + \phi_d(P_C - P_D)}, \tag{3}$$

where P<sub>C</sub> is the permeability of the polymeric matrix, P<sub>D</sub> is the permeability of the dispersed phase (MWNT-O), and Φ<sub>d</sub> is the volume fraction of the dispersed phase. Equation 3 assumes that the

MWNT-O is uniformly distributed over the free volume, reducing the space for permeation and favoring the sieving effect. The presence of intimate and complete interfacial contact between the two phases is also assumed. Furthermore, it was considered that  $PD = 0$  (assuming a good quality of the material walls) [6].

To calculate  $\Phi_d$  (Equation 4) for each of the MMMs, the density of the polymeric matrix (polysulfone) used was  $1.24 \text{ g/cm}^3$ , and the density of the dispersed phase (MWNT-O) was  $1.3 \text{ g/cm}^3$ .

$$\Phi_d = \frac{CNT(\text{wt.}\%) \cdot \left( \frac{\rho_{CNT}}{CNT(\text{wt.}\%)} + \frac{\rho_{PSf}}{PSf(\text{wt.}\%)} \right)}{\rho_{CNT}} \quad (4)$$

We used Microsoft Excel 2016 to verify the accuracy of the results obtained using Maxwell's model. The theoretical and experimental results were graphically compared. Permeability is determined by monitoring the increase in the pressure inside the permeate volume with time.

### 3. Results and Discussion

Figure 2 and Figure 3 present the images of the membranes. Clusters were not formed, and this was validated visually. The results revealed good dispersion of the fillers inside the polymeric matrix.



**Figure 2** Images of the symmetric MMMs containing a) 0 wt.%, b) 0.1 wt.%, c) 0.5 wt.%, and d) 1 wt.% of MWNT-O.



**Figure 3** Images of the asymmetric MMMs containing a) 0 wt.%, b) 1 wt.%, c) 3 wt.%, and d) 5 wt.% of MWNT-O.

$\text{CO}_2$  and  $\text{N}_2$  permeabilities for symmetric and asymmetric MMMs are shown in Table 1 and Table 2. Although the selectivity of polysulfone is usually high, the packaging of the polymeric chain can be tuned by controlling the nature of the preparation process. This eventually results in a change in the transport properties. The selectivity data obtained by us agreed well with the data reported in the literature [7].

**Table 1** Experimental and theoretical permeability achieved using MMMs.

MWNT-O (wt%)	CO <sub>2</sub> Permeability (Barrer)		N <sub>2</sub> Permeability (Barrer)		Selectivity <sup>a</sup> CO <sub>2</sub> /N <sub>2</sub>
	Experimental	Maxwell	Experimental	Maxwell	
0	12.0	12.0	3.3	3.3	3.6
0.1	11.0	12.0	3.2	3.3	3.4
0.5	13.0	12.0	1.5	3.3	8.7
1	6.0	12.0	0.4	3.3	15.0

<sup>a</sup> Ratio of permeabilities calculated from experimental permeability values (known as ideal selectivity).

**Table 2** Experimental and theoretical permeability achieved using asymmetric MMMs.

MWNT-O (wt%)	CO <sub>2</sub> Permeance (GPU)		N <sub>2</sub> Permeance (GPU)		Selectivity <sup>a</sup> CO <sub>2</sub> /N <sub>2</sub>
	Experimental	Maxwell	Experimental	Maxwell	
0	11.0	11.0	10.0	10.0	1.1
1	80.0	10.8	12.0	9.9	6.7
3	160.0	10.5	121.0	9.7	1.3
5	177.0	10.2	162.0	9.4	1.1

<sup>a</sup> Ratio of permeabilities calculated from experimental permeance values (known as ideal selectivity).

Analysis of the data presented in Table 1 reveals a noticeable change in CO<sub>2</sub> permeability when 0.5–1.0 wt.% of MWNT-O is used. However, little difference was observed for other cases. For the case of N<sub>2</sub> permeability, the lowest content of MWNT-O did not cause significant changes in membrane properties, but higher contents of the filler (0.5 and 1 wt.%) resulted in a decrease in the extent of permeation.

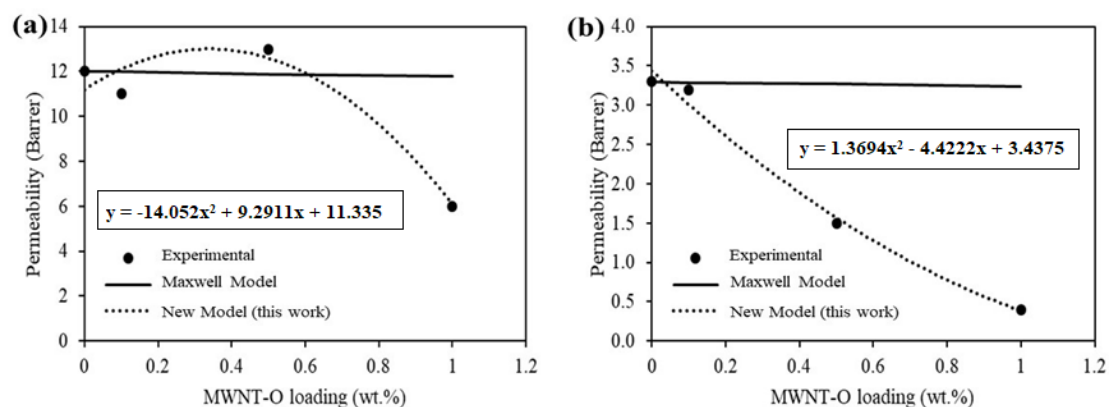
It is worth noting that the ideal selectivities increased from 3.6 to 15 with an increase in the filler content. In addition, it was noted that Maxwell’s model could effectively fit the experimental results under conditions of low filler contents. The results obtained under conditions of higher filler contents can be ascribed to the assumption that the permeability of the dispersed phase, P<sub>D</sub>, was zero. This should be true for defect-free MWNT-O systems. Under these conditions, some defects are generated in the fillers based on the synthetic or functionalization methods.

The decrease in permeability with an increase in the MMM filler content can be explained by the decrease in the free fraction volume of the membrane. This indicated a good dispersion of the filler into the polymeric matrix. Under these conditions, the gap between the filler and the polymer did not increase. The dense structure developed in the presence of the filler can result in a decrease in the free volume of the original polymer into which permeation occurs. This results in an increase in the packing density of the membrane.

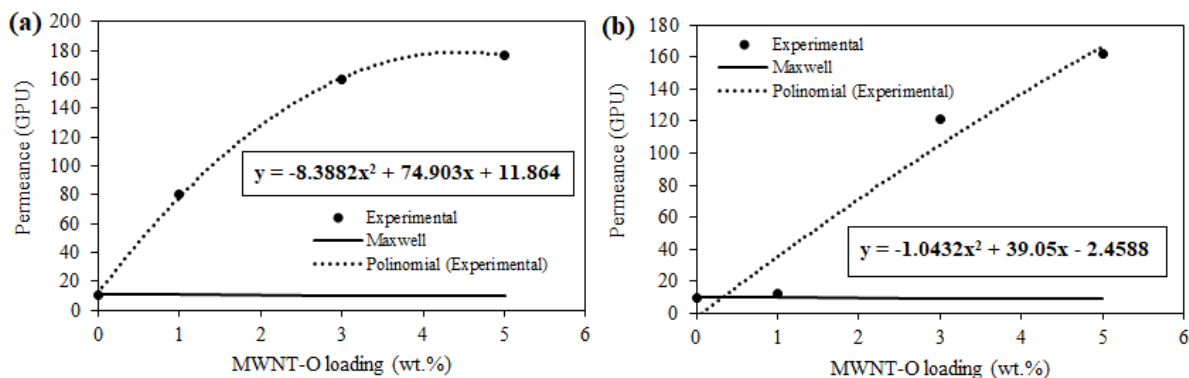
Analysis of the data in Table 2 reveals an increase in the gas permeability rate with an increase in the filler content. The increase can be attributed to an increase in the porosity of the filler in the membrane. The membrane thickness decreased from 50 to 5 mm, and this could be attributed to the changes in the morphology of the membrane (from symmetric to asymmetric). However, except for the case when 1 wt.% of MWNT-O was used, defects were formed in the membranes. This was

also revealed by the selectivities values. Analysis of the selectivity indicated that the Knudsen diffusion process predominantly contributed to the process of permeation. Selectivity is defined as the ratio between the square root of the molecular weights of the permeants. The selectivity of the membrane containing 1 wt.% of MWNT-O increased significantly, and it was higher than the selectivity of the membranes containing a large amount of filler loads. This indicated good dispersion of the functionalized nanotubes in the polymeric matrix. Although the permeance recorded for this system was higher than the permeance of the non-loaded membrane, the membrane selectivity was significantly high (6.7). However, the permeance was lower than the permeance of the symmetric membrane (15). This indicated that the free fraction volume recorded when the route of asymmetric membrane preparation was followed was higher than the free fraction volume recorded when the symmetric membrane preparation route was followed. Wijiyanti and coworkers prepared MMMs by dispersing zeolite-templated carbon (which were used as the fillers) into polysulfone membranes (used as hollow fibers) following the dry-jet wet spinning technique. The best result was recorded when 0.4 wt.% of the filler was used. The CO<sub>2</sub> and N<sub>2</sub> permeabilities were 58.5 and 5.0 GPU, respectively. The permeability was lower than the permeability recorded when 1 wt.% of MWNT-O was used. However, the ideal selectivity reported by them was higher than the ideal selectivity reported by us (11.7 against 6.7) [8]. Norouzi and collaborators [10] investigated MMMs based on the dispersion properties of TiO<sub>2</sub>/CNTs in polyurethane. When 0.5 wt.% of the filler was used, the CO<sub>2</sub> permeability was recorded to be 68.31, and the CO<sub>2</sub>/N<sub>2</sub> separation factor was 74.85.

It is difficult to achieve an extent of CO<sub>2</sub> permeation that is higher than the extent of N<sub>2</sub> permeation when carbon nanotubes functionalized with oxygen-containing groups are used. This can be attributed to the enhanced sorption ability of the permeant. The primary role of the filler was to increase the polymer packing density for symmetric membranes. Clusters were formed for asymmetric films. The changes in the membrane packing density and the extent of filler aggregation realized could not be described by the permeability model proposed by Maxwell, as the model assumes a good dispersion ability of the filler. Figure 4 and Figure 5 present the results obtained by comparing the experimental and theoretical data recorded for the gases. The results reveal a polynomial linear regression behavior for symmetric and asymmetric MMMs.



**Figure 4** Experimental and theoretical data reflecting the (a) CO<sub>2</sub> and (b) N<sub>2</sub> permeability of the symmetric MMMs.



**Figure 5** Experimental and theoretical permeance of asymmetric MMMs for (a) CO<sub>2</sub> and (b) N<sub>2</sub> permeation.

Figure 4 presents the experimental data and the curves fit using the model proposed by Maxwell. The results were obtained using a polynomial equation describing symmetric MMMs. The best fit was obtained for CO<sub>2</sub>. It was also observed that the polynomial model fit the data better than the Maxwell model.

Equation 5 and 6 presents the mathematical fit for CO<sub>2</sub> and N<sub>2</sub> permeability for the cases of symmetric MMMs, respectively. Here P denotes the permeability of the MMMs, and x is the MWNT-O content in wt.%.

$$P = -14.052x^2 + 9.2911x + 11.335 \tag{5}$$

$$P = 1.3694x^2 - 4.4222x + 3.4375 \tag{6}$$

The polynomial regression method was used to analyze the experimental results obtained for the gases. A high coefficient of determination (R-squared; 0.94 for CO<sub>2</sub> and 0.99 for N<sub>2</sub>) was obtained, indicating that the equation generated following the regression method explains the permeability data. Thus, the fit can be used to predict the permeability of the symmetric polysulfone-based MMMs containing 0–1 wt.% of MWNT-O.

Figure 5 presents the experimental data for permeance and the curves obtained using the Maxwell model and polynomial regression method. As expected, the Maxwell model did not efficiently fit the data as the model assumed a good dispersion of the filler [9]. Equation 7 and Equation 8 present the mathematical fit for the phenomena of CO<sub>2</sub> and N<sub>2</sub> permeance in asymmetric MMMs. Q denotes the permeance of the MMMs, and x denotes the MWNT-O content in wt.%.

$$Q = -8.3882x^2 + 74.903x + 11.864 \tag{7}$$

$$Q = -1.0432x^2 + 39.05x - 2.4588 \tag{8}$$

The polynomial regression method was used to analyze the experimental results obtained for the gases, and high coefficients of determination (R-squared; 0.99 for CO<sub>2</sub> and 0.94 for N<sub>2</sub>) were obtained. This indicated that the equation generated following the regression method could explain the permeation data. Thus, the model can be used to predict the permeance of the asymmetric polysulfone-based MMMs containing 0.0–5.0 wt.% of MWNT-O.



#### **4. Conclusions**

The preparation of symmetric and asymmetric polysulfone-based MMMs containing MWNT-O was investigated to understand the permeation behavior of CO<sub>2</sub> and N<sub>2</sub>. The model proposed by Maxwell could be used to effectively describe CO<sub>2</sub> permeation under conditions of low filler contents in MMM. The results indicated that the assumptions associated with the changes in the free volume fraction attributable to a well-dispersed phase were limited to this system and range. In general, the increase in the filler content for the case of the asymmetric membrane resulted in an increase in the polymer packing density. The permeability decreased, and the membrane selectivity increased. The use of asymmetric membranes helped increase the flux, and the high filler load resulted in the generation of defects in the membranes (exception: 1 wt.% MWNT-O). Analysis of the selectivity revealed that the permeation mechanism was dominated by the Knudsen diffusion process when the filler content was 0, 3, or 5 wt.%. Enhanced CO<sub>2</sub> sorption was not achieved for carbon nanotubes functionalized by oxygenated groups.

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#### **Author Contributions**

Thales – modelling of experimental data and paper writing, Marcelo – membrane preparation and permeation tests, Katia – supervision of the project, paper polishing, funds acquisition.

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#### **Competing Interests**

The authors have declared that no competing interests exist.

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