Enhancing gas permeability in mixed matrix membranes through tuning the nanoparticle properties

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A B S T R A C T

Mixed matrix membranes containing a variety of nanoparticles were fabricated by the solvent casting method using a commercial aromatic polyimide as the base polymer. All gas permeabilities increased with increasing particle loading with no reduction in the selectivity, reflecting adequate polymer/particle compatibility. Importantly, under such conditions the permeability enhancement depended only upon the pore volume within the particle, regardless of the particle chemistry or the morphology of the membrane structure. Remarkably, despite a range of membrane chemistries and filler loadings, this permeability enhancement could be readily described with a simple free volume relationship. The results suggest that nanoparticle porosity should be the focus of research into mixed matrix membrane structures. These results are likely to apply in all diffusivity dominated systems where the particle pore size is significantly larger than the penetrant size, as is the case with glassy polymers and many inorganic additives at low pressures.

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1. Introduction

Mixed matrix membranes (MMMs) have been considered since the 1970s as an effective approach to improve the performance of both gas separation and water treatment polymeric membrane systems [1–3]. In this approach, nano-particulate fillers are added into the polymer phase, generally causing an enhancement in permeability and/or change in penetrant selectivity. A large number of MMMs using zeolites [4], silicas [5–7], carbons [8–10], metal–organic frameworks (MOFs) [11], zeolitic imidazolate frameworks (ZIFs) [12–14] and porous organic polymers (POPs) [15] have been shown to be promising candidates for gas separation applications. However, these MMMs are normally tested in isolation and rarely compared to each other. In the present work, a comparative study of gas separation using MMMs containing a variety of different nanoparticles has enabled important new insights into the factors that impact membrane performance.

The particles need to be well dispersed to guarantee the separation performance. One of the critical issues for MMMs is the presence of interfacial defects around the particles, which are caused by particle aggregation and poor particle–polymer interaction [16]. Such defects in the membrane can significantly reduce the gas selectivity and are also often related to increases in permeability. Therefore, MMM research has focused not only on the improvement of gas separation performance but also the preparation protocols and particle modifications to prevent or control these interfacial defects [17].

A number of workers have used computational approaches to evaluate the effect of nanoparticle properties [18,19]. Their performance is also often predicted through mathematical models from the relatively simple Maxwell model [20] to others significantly more complex [21]. The Maxwell model [20] is considered appropriate for low particle concentrations

$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)} \right] \tag{1}$$

where P_{eff} is the effective permeability of the mixed matrix membrane, ϕ is the volume fraction and P the permeability of the dispersed (d) and continuous (c) phases respectively. The Bruggeman [22] (Eq. 2) and Lewis–Nielsen [23] (Eq. 3) models were introduced to model systems with higher particle loadings

$$\frac{P_{eff}}{P_c} = \frac{1}{(1-\phi_d)^3} \left[\frac{(P_{eff}/P_c) - \alpha}{1-\alpha} \right]^3 \tag{2}$$

$$\frac{P_{eff}}{P_c} = \frac{1 + 2\phi_d[(\alpha-1)/(\alpha+2)]}{1 - \phi_d\psi[(\alpha-1)/(\alpha+2)]} \tag{3}$$

where $\alpha = P_d/P_c$ and $\psi = 1 + [(1-\phi_m)/\phi_m^2]\phi_d$, in which ϕ_m is the maximum achievable volume fraction of the particles, which is

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affected by factors such as particle shape, size, size distribution, and agglomeration. Mahajan and Koros also reported a modified Maxwell model that accounted for interfacial defects (i) [16]

$$P = P_c \left[\frac{P_{eff} + 2P_c - 2(\phi_d + \phi_i)(P_c - P_{eff})}{P_{eff} + 2P_c + (\phi_d + \phi_i)(P_c - P_{eff})} \right] \qquad (4)$$

However, an experimental evaluation of the impact of particle properties across a wide range of different nanoparticles has never been reported. In this work, we report for the first time the gas permeation properties of a series of MMMs in a glassy polymer substrate to determine the dominant particle properties and explain the permeation using a simple free volume-based model.

2. Experimental

2.1. Materials

The base polymer material used as a host matrix in this research was Matrimid®5218 (3,3,4,4-benzophenone tetracarbox-ylicdianhydride-diaminophenylidane) polyimide purchased from Huntsman Advanced Materials Americas Inc., America, in a powdered state. This polyimide was purified by solution and re-precipitation using methanol (Analytical reagent, Chem-Supply, Australia) and dichloromethane (DCM, Analytical reagent, Chem-Supply, Australia) to remove impurities. Carbon nanoparticles (Product number; 699624 as Carbon A and 699632 as Carbon B), and zeolitic imidazolate framework (ZIF-8 (Zn(mim)$_2$, mim=2-methylimidazole), Basolite Z1200) as a filler phase were purchased from Aldrich Inc., America. Carbon C was produced from briquetted Victorian brown coal via mild steam activation at 800 °C for 90 min, in a fixed bed reactor under a flow of N_2/H_2O (3 L/min and 0.25 cm^3/min, respectively). Cu-BTC ([Cu$_3$(BTC)$_2$]$_3$H$_2$O, also known as HKUST-1 where BTC=benzene-1,3,5-tricarboxylate) and a triarylamine-based POP (POP-2) were prepared according to the previous literature [24,25]. All materials were dried at 100 °C under vacuum overnight to remove the moisture before use. The physical properties of the nanoparticles used in this study are summarized in Table 1.

2.2. Mixed matrix membrane preparation

MMMs were prepared by a solvent casting method. The loading of nanoparticles was varied from 0 to 30 wt% for carbon and metal-organic framework MMMs and 0–20 wt% for POP-2 based on the weight of polymer. The nanoparticle loading was calculated based on the following equation

$$\text{Filler loading(wt\%)} = \frac{w_{filler}}{w_{polymer} + w_{filler}} \times 100 \qquad (5)$$

where $w_{polymer}$ and w_{filler} are the weight of polymer and filler, respectively. Solutions of 3 wt% filler and 3 wt% polymer in DCM were prepared separately by physical stirring using a magnetic stir bar overnight at room temperature, and each solution was then treated under ultrasonication (Unisonics, Australia) for 30 min within an iced water bath to maintain the temperature close to ambient. After ultrasonication, both homogeneous solutions were mixed together
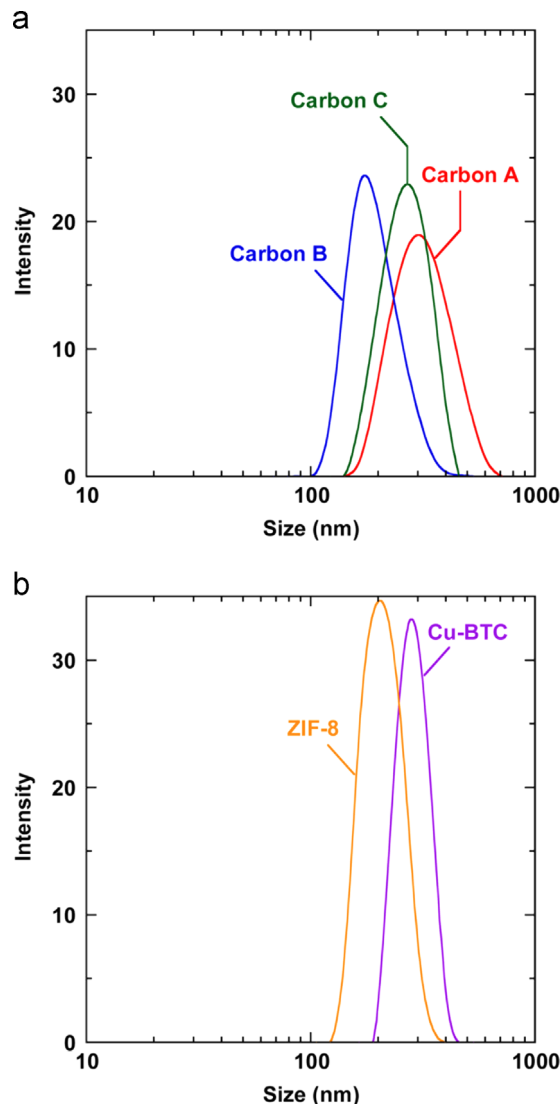

Fig. 1. Particle size distribution of the Carbons (a) and MOFs (b), measured using dynamic light scattering.

Table 1
Physical properties of the nanoparticles.

Property	Carbon A	Carbon B	Carbon C	POP-2 [25]	ZIF-8	Cu-BTC
Type	Carbon	Carbon	Carbon	POP	MOF	MOF
Surface area (m^2/g)[a]	77	252	540	781	1497 ± 32	1725 ± 150
Pore volume (cm^3/g)[a]	0.194	0.286	0.329	0.554	0.687 ± 0.015	0.762 ± 0.066
Pore size (Å)	137[b]	64[b]	20[a]	6, 10, 12.5	3.4, 11.6 [13]	3.5, 9.0 [31]
Particle size (nm)[c]	290	180	260	< 300	210	280
Density (g/cm^3)	1.828[b]	1.887[b]	1.90	1.33	0.95 [13]	1.05 ± 0.17 [29–31]
Water uptake (wt%)[d]	2.2	3.4	4.0	1.9	5.0	7.8

[a] Determined from N_2 BET sorption analysis.
[b] Cited from supplier information.
[c] Average particle size of Carbons (A, B, and C) and MOFs (ZIF-8 and Cu-BTC) were measured by dynamic light scattering, while for POP-2 this was estimated from the SEM images.
[d] For a 20 wt% MMM at 35 °C.