Can the addition of carbon nanoparticles to a polyimide membrane reduce plasticization?

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ABSTRACT

Mixed matrix membranes (MMMs) for carbon dioxide (CO_2) separation composed of a commercial aromatic polyimide as a host matrix and carbon nanoparticles as a filler phase have been prepared by a casting method. The solubility of CO_2 in the MMM could be predicted within error from the pure component isotherms, suggesting that the sorption of polymer to the nanoparticles did not significantly reduce the availability of sites for CO_2 to adsorb. The CO_2 permeability increased with filler loading without a reduction in the gas selectivity, reflecting the increase in fractional free volume provided by the carbon nanoparticles. This was reflected in significant changes in the CO_2 diffusivity. However, contrary to prior work, the use of the carbon nanoparticles was unable to reduce the effects of plasticisation by either CO_2 or water. Changes in the permeability of both water vapor and carbon dioxide occurred with time, particularly for relative humidities beyond 60%. The lack of plasticization resistance may reflect the use of sub-micron nanoparticles rather than larger ones.

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1. Introduction

Membrane technology is an attractive approach to gas and vapor separation due to its ease of operation, energy efficiency and cost-effectiveness, relative to other techniques such as solvent absorption, adsorption, and cryogenic distillation [1]. Polymer membrane-based separation technologies have been applied in industrial applications including natural gas sweetening, hydrogen recovery and oxygen enrichment. They are also seen to have potential for post combustion capture of carbon dioxide. However, there is a well-known trade-off in dense polymer membranes between gas permeability and selectivity for any given pair of components [2]. One of the effective ways to overcome this trend is to use mixed matrix membranes (MMMs) which combine the benefits of both polymer substrates and organic and/or inorganic fillers [3,4]. To date, a large variety of mixed matrix membranes using carbon nanotubes, carbon molecular sieves [5,6], activated carbon [7–9], zeolites [10], silica [11–13], and metal organic frameworks (MOFs) [14–16] have been investigated for gas separation applications. These systems are attractive because of their enhanced thermal, chemical, and mechanical stability in addition to their improved gas permeation, when compared to homogeneous polymer membranes.

Some workers have shown that the addition of fillers such as metal organic frame works (MOFs) [17], mesoporous silica [18] and zeolites [19] can suppress high pressure CO_2-induced plasticization. This is a phenomenon often observed in glassy polymers where the polymer matrix expands rapidly beyond a critical penetrant pressure, referred to as the plasticization pressure. It is claimed that the fillers used in mixed matrix systems enhance the interaction between polymer and fillers and thus act as pseudo-crosslinkers. However, other workers find the addition of ZIF-8 nanoparticles ineffective in reducing CO_2 plasticisation, unless a cross-linkable moiety is specifically added [20].

Carbon membranes have also been widely investigated as homogeneous systems derived from polymer precursors [21–23]. For example, we have previously reported the performance of microporous (diameter, $d < 2$ nm) carbon membranes for carbon dioxide (CO_2) capture [24]. Gas adsorption and molecular simulation experiments suggested that CO_2 is more readily adsorbed on microporous carbon than methane (CH_4) and nitrogen (N_2) [25]. Further, it has been shown that the selectivity of carbon membranes for more strongly adsorbed molecules such as CO_2 can be enhanced beyond that in a polymeric system by surface diffusion [26]. Indeed, in some cases, more of the diffusing species can migrate in the surface layer than through the pore volume [27]. Importantly, we have also shown that carbon membranes are resistant to the impact of a range of gas impurities, including

water, which is the most common contaminant in post-combustion capture [28].

In our more recent work, we have also shown that carbon nanoparticles can be similarly effective in improving the gas separation performance in mixed matrix systems [29,30]. Further, these particles are likely to be available at more moderate cost than additives such as metal organic frameworks (MOFs). In this work, we expand on these results to provide a more detailed analysis of the effectiveness of carbon-based mixed matrix systems across a range of operating pressures and water vapor humidities. A specific focus of the manuscript is to determine whether the addition of these nanoparticles can reduce plasticization of the membrane by both water vapor and CO_2, thus providing a material that provides for more stable operation in the field, with no loss in separation performance.

2. Experimental

2.1. Materials

The base polymer material used as host matrix in this research is Matrimid®5218 (3,3,4,4-benzophenone tetracarboxylicdianhydride-diaminophenylidane) polyimide purchased from Huntsman Advanced Materials Americas Inc, America, in a powder state. This polyimide was purified by dissolution in dichloromethane (DCM, Analytical reagent, Chem-Supply, Australia) and re-precipitation using methanol (Analytical reagent, Chem-Supply, Australia) to remove impurities. Carbon nanoparticles were purchased from Sigma-Aldrich Inc., America. The physical properties of the carbon nanoparticles are summarized in Table 1. Both the polyimide and carbon nanoparticles were dried at 100 °C overnight under vacuum to remove moisture before use.

Pure gases (O_2, N_2, CO_2, and CH_4) and gas mixtures (10% CO_2 in CH_4 and 10% CO_2 in N_2) were purchased from Coregas Australia with at least 99.5% purity.

2.2. Mixed matrix membrane preparation

Separate solutions of dichloromethane containing 3–4 wt% of nanoparticles and 3–4 wt% of polymer were prepared. These separate solutions were stirred overnight at room temperature and then sonicated (Unisonics, Australia) for 30 min within an ice bath. The two solutions were mixed together in different proportions and then again treated by physical stirring overnight and ultrasonication for 30 min.

Base Matrimid® membranes and mixed matrix membranes of different filler loadings (10, 20, and 30 wt% nanoparticles) were prepared from such solutions by a standard casting method [31]. A homogeneous polymer/filler solution was cast onto a glass petri dish which was covered to prevent contamination and left at room

Table 1
Physical properties of the carbon nanoparticles.

Property	Carbon
Average particle size (nm)[a]	180
Surface area (m^2/g)[b]	252
Pore volume (cm^3/g)[b]	0.286
Average pore diameter (Å)[c]	64
Absolute density (g/cm^3)[c]	1.887
Free volume[d]	0.540

[a] From dynamic light scattering.
[b] Determined from N_2 BET sorption analysis.
[c] Manufacturer information.
[d] Calculated in this work from the particle pore volume and density.

temperature for 24–48 h. The homogeneous membranes were then removed from the petri dish using a small amount of distilled water. The membrane was placed in a vacuum oven at 35 °C for 24 h and further dried at 100 °C for 24 h. The thickness of the well-dried membrane varied from 60 to 80 μm, as measured by a micrometer (MDC-25MX, Mitsutoyo, Japan), giving an accuracy of ±1 μm.

The volume fraction of carbon particle (ϕ_{filler}) in the membrane was calculated using the following equation:

$$\phi_{filler} = \frac{w_{filler}}{w_{filler} + \frac{\rho_{filler}}{\rho_{polymer}}(1 - w_{filler})} \tag{1}$$

where w_{filler} is the weight fraction of carbon particle added to the membrane. $\rho_{polymer}$ and ρ_{filler} are the density of polymer and carbon particle, respectively.

2.3. Characterization

The membrane density (ρ) was determined based on the Archimedean principle at room temperature (24 ± 1 °C) [32]. Dense membranes were weighed using an analytical balance (Mettler Toledo AB204-5) in air (w_{air}) and then in ethanol (Undenatured AR 100%, Chem-Supply, Australia) (w_{EtOH}). This experiment was performed repeatedly using several different membranes to ensure reproducibility. As a comparison, the theoretical density (ρ_{theory}) of the MMMs was calculated using the following equation:

$$\rho_{theory} = \frac{1}{\frac{1 - w_{filler}}{\rho_{polymer}} + \frac{w_{filler}}{\rho_{filler}}} \tag{2}$$

The difference between the theoretical and the experimental density (ρ_{exp}), provides an indication of the additional voids created between the nanoparticles and the surrounding polymer [33]. This void volume fraction, or additional free volume, ϕ_{Void} can be estimated from:

$$\phi_{Void} = 1 - \left(\frac{\rho_{exp}}{\rho_{theory}}\right) \tag{3}$$

The FFV of dense polymeric membranes can be characterized by the following equation;

$$FFV = \frac{V - 1.3V_W}{V} \tag{4}$$

where V is the specific volume of polymer, and V_w is the van der Waals volume [34–36]. The FFV value calculated for pure Matrimid using this approach was 0.167. The FFV of the carbon was determined in our previous work from the pore volume and the particle density as 0.540 [29,30]. The FFV of the ideal MMM is then expressed as Eq. (5):

$$FFV = FFV_{polymer}(\phi_{polymer}) + FFV_{filler}(\phi_{filler}) \tag{5}$$

When the MMM includes a significant void volume fraction, the total FFV becomes that shown in Eq. (6):

$$FFV = FFV_{polymer}(\phi_{polymer}) + FFV_{filler}(\phi_{filler}) + \phi_{voids} \tag{6}$$

A differential scanning calorimeter (DSC8500, Perkin Elmer, Shelton USA) was used to measure polymer glass transition temperature, T_g. Samples were heated over the temperature range of 50–400 °C at a rate of 10 °C/min under nitrogen. T_g was determined as the midpoint of the slope change in the second heating scan.

Wide-angle X-ray diffraction (WAXD) measurements were performed on a D8 advance (Bruker, Germany) at 5 seconds per step of 0.02° using a Ni-filtered CuKα radiation source at 40 kV and 30 mA. The dispersion angle was between 5 and 50°. The d-spacing, which