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

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Abstract

Mixed matrix membranes (MMMs) for carbon dioxide (CO₂) 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 CO₂ 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 CO₂ to adsorb. The CO₂ 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 CO₂ diffusivity. However, contrary to prior work, the use of the carbon nanoparticles was unable to reduce the effects of plasticisation by either CO₂ 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.

Keywords: Mixed matrix membrane; Carbon dioxide; Polyimide; Carbon; Plasticization

1. INTRODUCTION

Membrane technology is an attractive approach to gas and vapour 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 frameworks (MOFs)[17], mesoporous silica [18] and zeolites[19] can suppress high pressure CO₂-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 CO₂ 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 (CO₂) capture.[24] Gas adsorption and molecular simulation experiments suggested that CO₂ is more readily adsorbed on microporous carbon than methane (CH₄) and nitrogen (N₂).[25] Further, it has been shown that the selectivity of carbon membranes for more strongly adsorbed molecules such as CO₂ 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 CO₂, 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 tetracarboxylic dianhydride-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 (O₂, N₂, CO₂, and CH₄) and gas mixtures (10% CO₂ in CH₄ and 10% CO₂ in N₂) 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 minutes 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 minutes.

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 temperature for 24-48 hours. 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 hours and further dried at 100°C for 24 hours. 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 $\pm 1\mu\text{m}$.

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

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

where w_{filler} is the weight fraction of carbon particle added to the membrane. ρ_{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 ($24 \pm 1^\circ\text{C}$).^[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:

$$\rho_{\text{theory}} = \frac{1}{\frac{1 - w_{\text{filler}}}{\rho_{\text{polymer}}} + \frac{w_{\text{filler}}}{\rho_{\text{filler}}}} \quad (2)$$

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:

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

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

$$FFV = \frac{V - 1.3V_w}{V} \quad (4)$$

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 Equation (5):

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

When the MMM includes a significant void volume fraction, the total *FFV* becomes that shown in Equation 6:

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

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 CuK α radiation source at 40 kV and 30 mA. The dispersion angle was between 5 and 50°. The d -spacing, which represents the mean distance between polymer chains, was calculated using Bragg's Law (Equation 7);

$$\lambda = 2d \sin\theta \quad (7)$$

where λ is the wavelength of the radiation, 1.54 Å, and 2θ is the maximum intensity in a halo peak.

2.4. Pure and mixed gas permeation

The pure gas permeability of O₂, N₂, CO₂, and CH₄ were determined by the constant-volume/variable-pressure (CVVP) method, which measures the steady-state gas flux through a membrane of known thickness under a given pressure difference.[37] The gas permeation measurement is performed with a leak rate of below 1.0×10⁻⁶ torr/s, which is negligible in the case of well dried defect free samples. Pure gas permeation data were determined at 35 °C and 2 atm feed gas pressure using a minimum of two membrane samples to ensure the reproducibility of the experimental results. The gas permeation coefficient P (barrer = × 10⁻¹⁰ cm³ (STP)cm/(cm²·s·cmHg)) was determined from the slope of the time-pressure curve at steady state.

Gas permeability in both pure CO₂ and CH₄ and in mixtures of 10% CO₂ in CH₄ was also determined at 35°C for a sequence of pressures from 2 to 10 atm using a constant-pressure/variable-volume (CPVV) apparatus designed and built in-house.[38, 39]. In addition, the permeability in humid gas mixtures of 10% CO₂ in CH₄ and 10% CO₂ in N₂ were recorded using this approach across a range of humidities at a total feed gas pressure of 7.5 atm. The gas permeability was recorded one hour after stabilization at each pressure. For these CPVV experiments, the flux of each gas component (J_i) passing through the membrane was evaluated by:

$$J_i = \frac{Q \cdot x_i}{A} \quad (8)$$

where Q is the total permeate flowrate (cm³(STP) s⁻¹), x_i is the mol fraction of the gas in the permeate stream and A is the effective membrane area (cm²). The permeate mol fractions were determined by gas chromatography (CP-3800, Varian, Inc., Australia). The permeability of each gas component was then determined from Equation 9:

$$P_i = \frac{J_i \cdot \ell}{(p_{i,feed} - p_{i,permeate})} \quad (9)$$

where $p_{i,feed}$ and $p_{i,permeate}$ the partial pressure (kPa) of component i on the feed and permeate side of the membrane respectively and ℓ is the membrane thickness.

The ideal gas selectivity (α (A/B)) of gas A over gas B was expressed as the ratio of their permeability coefficients (P_A and P_B) (Equation 10).

$$\alpha(A/B) = \frac{P_A}{P_B} \quad (10)$$

2.5. CO₂ sorption

CO₂ sorption measurements were conducted on a Rubotherm magnetic suspension balance (Rubotherm GmbH, Germany) at 35°C and up to 40 atm. The sample was loaded into the chamber and evacuated at 35°C for at least 12 hours prior to each experiment. The chamber was dosed with gas to the desired pressure and equilibrated at each pressure for 30 minutes. Thermal equilibrium due to adiabatic compression of the gas was generally achieved within 10 minutes. The volume of the system was determined via helium measurement to correct for any changes in buoyancy due to the change in gas pressure. The CO₂ sorption isotherm was characterized using the dual-mode sorption model according to Equation 11:[36]

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (11)$$

where C_H is the gas concentration in the Langmuir-type hole filling sites and C_D is the concentration in the equilibrium or Henry's Law regions. The sorption coefficient in these equilibrium regions is k_D (cm³ (STP) / (cm³(polymer atm)), b is the Langmuir affinity parameter (1/atm), and C'_H is the Langmuir capacity parameter (cm³ (STP) / (cm³(polymer))). For the carbon nanoparticles, the Henry's Law concentration was set to zero.

3. RESULTS AND DISCUSSION

3.1. Characterization

The membrane density of the base Matrimid is measured as $1.223 \pm 0.019 \text{ g/cm}^3$, which is in good agreement with the literature.[40] The density of the carbon nanoparticle is given by the manufacturer as 1.887 g/cm^3 . Figure 1 presents the effect of filler loading on the membrane density of MMMs formed from the mixing of these two materials. The difference between the experimental and theoretical densities can be characterized by defining a void volume fraction (ϕ_{voids}) as expressed in Equation (3) [33].

As presented in Figure 1(a), the difference between experimental and theoretical densities increased with the filler loading suggesting either a slight error in the reported density of the filler, or the development of a small amount of free space between the carbon nanoparticles and the polymer phases (0 - 2 vol% of the total membrane sample).[29] This generation of additional free volume is well known to occur in mixed matrix systems.[33, 41]. The effect of this additional free volume upon the total free volume is shown in Figure 1(b), using Equations 5 and 6.

Figure 2 presents the relationship between the glass transition temperature and filler loading. The T_g of the base Matrimid was 310°C which is consistent with the literature values.[42] The T_g of MMMs increases from 315°C to 319°C with increasing filler loading, indicating that the membrane becomes more rigid as the carbon particles are incorporated. This is consistent with visual observations of the membranes becoming less flexible and more brittle as the loading increased. Similar results of this increase in T_g of MMMs has been reported for Matrimid-based MMMs with carbon molecular sieves (CMS) and MOFs.[5, 43]

Figure 3 presents the WAXD profile of the composite membranes and carbon. All profiles showed broad peaks indicating that these are not crystalline structures but in an amorphous state. The d -spacing of Matrimid was $5.7 \text{ \AA}$ ($2\theta = 15.4^\circ$) which is in good

agreement with the literature.[44] This peak persists in the mixed matrix systems, suggesting that the carbon nanoparticles, while increasing polymer rigidity, did not significantly affect the distance between polymer segments. Peaks for the carbon were observed at 25° (d -spacing = 3.6 Å) and 43° (d -spacing = 2.1 Å). Interestingly, the peak at 25° appears to shift to a smaller pore size (30° , d -spacing = 3.0 Å) in the mixed matrix membranes. This change in peak position may relate to the penetration of polymer chains into these pores[45], or it may simply reflect variability within the carbon nanoparticles themselves. However, it should be noted that the WAXD analysis covers only a very limited range of void sizes. The manufacturer indicates that the average pore size of the carbon is 64 Å, which is well outside the range considered here.

3.2. Pure and mixed gas permeation and separation

Figure 4 presents the effect of filler loading on the single dry gas permeability and selectivity of the mixed matrix membranes at 2 atm and 35°C , which is a typical condition of post-combustion capture. The values for pure Matrimid are in good agreement with literature values.[46] All gas permeabilities increase with the loading of carbon and in the order CO_2 (kinetic diameter: 3.30 Å) > O_2 (3.46 Å) > N_2 (3.64 Å) > CH_4 (3.80 Å), regardless of the carbon loading.[47] This order reflects the kinetic diameter of each penetrant as expected for a diffusivity selective glassy polymer [48]. Conversely, there is little, if any, change in the gas selectivities for any gas pair. This type of behavior has been reported previously for mixed matrix systems [14, 49, 50] and in our own earlier reports [29, 30] and reflects the increasing *FFV* in the membranes provided by the nanoparticles (Figure 1).

Figure 5 presents the pressure dependence of the pure and mixed CO_2 and CH_4 permeability of the mixed matrix membranes. The dry pure gas permeabilities decrease with increasing total feed pressure. This is typical behavior of glassy polymer membranes owing

to the decrease in solubility.[51] However, when the feed pressure reaches 10 atm, the pure CO₂ permeability increases, indicating CO₂-induced plasticization. This plasticization pressure is consistent with other workers for Matrimid.[51, 52] Furthermore, the CO₂ permeability becomes time dependent at this pressure. Importantly, the addition of the carbon nanoparticles was unable to prevent the onset of plasticization at the plasticization pressure, or to reduce the rate of plasticization in the following ten hours (see Figure 6). This is in contrast to other workers who have shown that the addition of nanoparticles to a polymer acts to prevent plasticization. [17-19]

The CO₂ permeability under dry mixed gas conditions is identical within the error margins to the pure gas data below 10 atm total feed pressure. This reflects the fact that while the lower CO₂ partial pressure should lead to a higher pure gas solubility, the presence of the methane provides competition for these Langmuir sorption sites[53]. However, no plasticization is observed at 10 atm feed pressure. The CO₂ permeability continues to decrease because the partial pressure of CO₂ (1 atm) is much lower than that of pure CO₂ at 10 atm.

3.3. CO₂ sorption

Figure 7 presents the sorption isotherms of the base Matrimid, the carbon nanoparticles, and the 20wt% mixed matrix membrane. The CO₂ sorption isotherms in Matrimid and the 20wt% membranes were concave to the pressure axis, indicating typical dual-mode sorption behavior. The CO₂ uptake of carbon is greater than that of Matrimid, suggesting that the CO₂ uptake of the mixed matrix membranes will increase with filler loading as is observed for the 20 wt% membrane. The dual-mode sorption parameters of Matrimid, determined from Equation 5 are slightly different to those in the literature.[40, 54, 55] (see Table 2). This reflects differences in the casting solvent and annealing conditions.[51] A simple Langmuir sorption isotherm can be used to model the carbon nanoparticle. The C'_H of the carbon particle is significantly

larger than that of Matrimid, but similar to that observed for other activated carbons (Table 2).[56]

If an additive model is assumed, the CO₂ concentration in the mixed matrix membranes can be expressed simply as:

$$C = \phi_{filler} C_{filler} + (1 - \phi_{filler}) C_{polymer} \quad (12)$$

where C_{filler} and $C_{polymer}$ are the concentrations of CO₂ in the filler and polymer, respectively. This equation provides a good fit to the MMM curve within experimental error, as presented in Figure 7. This indicates that the available sites for CO₂ sorption to the nanoparticles are not reduced significantly from polymer adsorbing to their surface.

The average diffusion coefficient, D_{ave} can be estimated from the concentrations at the feed (1) and permeate (2) faces of the membrane:

$$P = \frac{D_{ave} (C_1 - C_2)}{p_1 - p_2} \quad (13)$$

By setting $C_2=p_2=0$, the average diffusion coefficient can be determined from the solubility based on the upstream conditions ($S_1 = C_1/p_1$). Figure 8 presents the resulting CO₂ diffusion coefficients of the base Matrimid and 20wt% mixed matrix membrane as a function of feed pressure at 35°C. The diffusion coefficients of all membranes increased with increasing feed pressure. This suggests that membrane swelling is in fact occurring to some extent at all feed pressures, rather than just above the plasticization pressure, where polymer relaxation becomes dominant. The infinite dilution diffusion coefficient, D_0 is obtained from the extrapolation of these lines gives 5.45×10^{-9} cm²/s for Matrimid, which is within the range of values predicted by other authors [57-59]. The diffusivity increases to 8.90×10^{-9} cm²/s for the 20wt% MMM, respectively, reflecting the increased fractional free volume from the incorporation of carbon particles. However, there is again no evidence of any reduction in membrane swelling from the addition of nanoparticles.

Figure 9 presents the water vapor permeability through Matrimid and the 20wt% MMM as a function of water activity in a CH₄/CO₂ mixture at 35°C and 7.5 bar. The water permeability of both membranes slightly increases at water activity of 0.2-0.6 due to increasing water sorption. Beyond these activities it the permeability increases more rapidly due to the plasticization by water.[39] The water vapor permeability of the MMM is slightly higher than that of Matrimid across all water activities. Importantly, the nanoparticles are again unable to restrict the effects of plasticization.

Figure 10 presents the changes in the permeability of CO₂ and N₂ through a 20wt% MMM as a function of time in N₂/CO₂ mixture at 35°C, 7.5 bar and a water activity $\alpha > 0.9$. As shown in our prior work, the permeability and selectivity under dry conditions is higher than under humid conditions due to competitive sorption. However, once the membranes are exposed to humid conditions, the permeability increases gradually and the selectivity decreases with time, again reflective of plasticization due to the presence of water vapor. The CO₂ permeability after 7 days was 14 % greater, while the selectivity of CO₂/N₂ were 12% lower than that of the initial performance (0 days). This again shows that the carbon nanoparticles are ineffective in limiting plasticization effects.

A possible reason for the lack of plasticization resistance could be a weak interaction between the polymer and the carbon nanoparticles that does not facilitate a pseudo-crosslinking role. Alternatively, it may reflect the impact of nanoparticle size. The particles here are typically 0.18µm in size [29]. Askari *et al.*[20] also used sub-micron particle sizes (0.02 – 0.08 µm) and did not observe any reduction in plasticization unless the nanoparticles were chemically crosslinked to the polymer. Conversely, workers who do see a reduction in plasticization use particles of micron or greater size (Shahid *et al.* uses < 5 µm [17], Adams *et al.* uses 0.5 to 1.5 µm [19] and Khan *et al.* uses 1- 2 µm [18]). These larger particle sizes will alter the way that the polymer can increase in free volume during the plasticization process.

4. CONCLUSION

We have prepared dense polyimide-carbon MMMs containing up to 30 wt% loading by a casting method. The experimental densities of the MMMs were only slightly lower than those theoretically predicted, suggesting that interfacial gaps between the polyimide and particles were small. The CO₂ solubility for the MMM system was readily predicted from the sorption isotherms of the individual components, indicating that the availability of sorption sites was not reduced by their interactions. The CO₂ permeability increased with carbon loading without a reduction in the gas selectivity, reflecting the increase in fractional free volume provided by the carbon nanoparticles. The CO₂ diffusivity also increased in line with the increase in fractional free volume afforded by the nanoparticles. The presence of water vapor in the feed gas stream reduced the membrane performance due to competitive sorption and caused membrane plasticization. Contrary to work presented by other researchers, the addition of carbon nanoparticles was unable to reduce the effects of plasticization by either CO₂ or water vapor. We speculate that this reflects the small, sub-micron particle sizes used here, relative to the larger particles used by other workers.

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Figure Captions

- Figure 1 (a) The effect of filler loading on the membrane density where the solid lines represent the best fit to the experimental data while the dashed lines represent Equation (2). (b) the effect of the void volume generated between the nanoparticles and the polymer on the fractional free volume (*FFV*) where Equation (5) gives the results without a void fraction and Equation (6) includes this void volume.
- Figure 2 Effect of filler loading on the polymer glass transition temperature.
- Figure 3 WAXD profiles of Matrimid, carbon-based mixed matrix membranes, and pure carbon nanoparticles.
- Figure 4 Effect of filler loading on (a) dry pure gas permeability and (b) pure gas selectivity of MMMs using carbon determined by CVVP method.
- Figure 5 Dry pure and mixed CO₂/CH₄ permeability in Matrimid and 20 wt% mixed matrix membrane as a function of total feed pressure at 35°C determined by the CPVV method. Solid and dashed lines represent pure and mixed gas data, respectively.
- Figure 6 The time dependence of the increase in CO₂ permeability at 10 bar feed pressure and 35°C for pure CO₂ (normalized to the permeability after one hour) in pure Matrimid and the 20wt% mixed matrix membrane. Results determined by the CPVV method.
- Figure 7 CO₂ sorption isotherms for Matrimid, pure carbon, and a 20 wt% mixed matrix membrane. The solid lines represent the best fit to the dual mode sorption model (Equation (11)).
- Figure 8 Average diffusion coefficients in Matrimid and 20 wt% mixed matrix membrane as a function of feed pressure at 35°C.

Figure 9 Water vapor permeability Matrimid and 20 wt% mixed matrix membrane as a function of feed water activity at 35°C and 7.5 bar in a mixture of 10% CO₂ in CH₄.

Figure 10 The permeability of a 20 wt% mixed matrix membrane in a gas mixture of 10% CO₂ in N₂ at 7.5 bar and 35°C as a function of time under both dry conditions and at a humidity of $\alpha > 0.9$.

Table Captions

Table 1 Physical properties of the carbon nanoparticles.

Table 2 Dual mode sorption parameters of the carbon nanoparticles, the MMM (20wt%) and pure Matrimid.

Figure 1 (Kanehashi *et al.*)

Figure 2 (Kanehashi *et al.*)

Figure 3 (Kanehashi *et al.*)

Figure 4 (Kanehashi *et al.*)

Figure 5 (Kanehashi *et al.*)

Figure 6 (Kanehashi *et al.*)

Figure 7 (Kanehashi *et al.*)

Figure 8 (Kanehashi *et al.*)

Figure 9 (Kanehashi *et al.*)

Figure 10 (Kanehashi *et al.*)

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 N₂ BET sorption analysis

(c) Manufacturer information

(d) Calculated in this work from the particle pore volume and density

Table 2 Dual mode sorption parameters of the carbon nanoparticles, the MMM (20wt%) and pure Matrimid

Sample	k_D cm^3 (STP)/ cm^3	C'_H cm^3 (STP)/ cm^3	mmol/g	b atm^{-1}
Carbon	–	158 ± 15	3.7 ± 0.3	0.060 ± 0.013
Activated Carbon [56]	–	–	6 – 20	0.057 - 0.12
MMM (20wt%)	1.76 ± 0.04	37.4 ± 1.6	–	0.41 ± 0.04
Matrimid	1.59 ± 0.12	36.0 ± 4.0	–	0.49 ± 0.15
(a) Matrimid [40]	1.42	35.0	–	0.702
(b) Matrimid [54]	1.44	25.5	–	0.367

- Mixed matrix membranes(MMM) prepared from carbon nanoparticles in Matrimid
- CO₂ solubility isotherms for MMM predicted by simple addition of component isotherms.
- CO₂ diffusivity increased uniformly as a result of additional free volume.
- Nanoparticles were unable to prevent plasticisation by water or CO₂
- The use of sub-micron nanoparticles may relate to the lack of plasticisation resistance.