

## Pebax-1657 Nanocomposite Membranes Incorporated with Nanoparticles/Colloids/Carbon Nanotubes for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> Separation

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**ABSTRACT:** Pebax-1657 is known as a promising polymeric membrane material for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separation. In order to further improve its gas separation performance and reinforce the membrane, different fillers including silica nanoparticles, polystyrene (PS) colloids, and carbon nanotubes (CNTs) were incorporated into the polymer matrix to form nanocomposite membranes. The nanocomposite membranes of Pebax-1657/silica and Pebax-1657/PS colloid had a decreased CO<sub>2</sub> permeability and selectivity over N<sub>2</sub> or H<sub>2</sub> compared to the pure Pebax-1657 membrane, while the Pebax-1657/CNT nanocomposite membranes had an increased CO<sub>2</sub> permeability, retaining similar CO<sub>2</sub>/N<sub>2</sub> or CO<sub>2</sub>/H<sub>2</sub> selectivity compared to the pure polymer membrane. The CO<sub>2</sub> permeability increased with increasing CNT content and reached a maximum at 5 wt % CNTs. The CNT-enhanced gas permeability was attributed to the increase in gas diffusivity. The tensile modulus of Pebax-1657 increased 43% after adding 5 wt % single-wall CNTs (SWNTs), and increased 24% after adding 5 wt % multi-wall CNTs (MWNTs). Thus, it is feasible to add CNTs to Pebax-1657 membranes for improved mechanical strength and gas separation performance. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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### INTRODUCTION

Gas separation through polymer membranes is reckoned to be an effective approach for the separation of gaseous mixtures accounting for high separation efficiency, low running costs, and simple operating procedures compared to conventional separation methods.<sup>1–5</sup> Hence, there is an increasing demand to develop polymeric membrane materials with high selectivity and permeability for various gas separation applications. However, polymeric membranes generally undergo a trade off limitation between permeability and selectivity as shown in the upper bound curves developed by Robeson.<sup>6</sup> Physical modifications have been done through incorporation of fillers such as silica, zeolite, titanium dioxide, alumina, carbon black, and other materials into polymer matrices.<sup>7–12</sup> Compared to pure polymer membranes, some of the polymer/filler nanocomposite membranes show improved permeability without sacrificing gas selectivity, or even improved selectivity.<sup>13–15</sup> Polymer membranes have also been chemically modified by blocking, grafting, cross-linking, and other methods, which change the

composition and structure of the macromolecules and may lead to improvements in gas separation properties.<sup>16–19</sup>

Block copolymers with immiscible soft and rigid blocks like polyether-*block*-polyamide (Pebax) have been shown as promising membrane materials for gas separation.<sup>20–22</sup> Pebax is a thermoplastic elastomer combining linear chains of the hard polyamide (PA) segments such as nylon-6 (PA-6) and nylon-12 (PA-12) that provide mechanical strength with interspacing of flexible polyether (PE) segments such as polyethylene oxide (PEO) and poly(tetramethylene oxide) (PTMEO) which offer excellent properties for gas separation.<sup>23–25</sup> Different type of Pebax copolymers have been manufactured by changing PE and PA compositions in the structure.<sup>26–28</sup> For example, the Pebax-4011 is a copolymer comprising 57 wt % of PEO and 43 wt % PA-6, while Pebax-1074 is a copolymer comprising 55 wt % of PEO and 45 wt % PA-12. Freeman et al.<sup>29</sup> studied the solubility of CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and He in Pebax-1074 and Pebax-4011 copolymers, and found as PEO composition in the copolymers increased, gas solubility increased. Lee et al.<sup>30</sup> studied the gas

separation properties of different type of Pebax materials, and found the Pebax-1657 copolymers showed a particular high selectivity for polarizable/nonpolar gas pairs such as CO<sub>2</sub>/N<sub>2</sub> and SO<sub>2</sub>/N<sub>2</sub>. In order to further improve its gas separation properties, nanocomposite membranes have been investigated by doping Pebax with different fillers. For instance, Zoppi et al.<sup>31</sup> observed a significant increase of selectivity for CO<sub>2</sub>/N<sub>2</sub> after incorporation of 20 wt % TiO<sub>2</sub> particles in Pebax matrix via *in situ* sol-gel process. Sridhar et al.<sup>32</sup> prepared cross-linked Pebax/MWNT nanocomposite membranes using 2,4-toluylene diisocyanate (TDI) as cross-linker, and found the selectivity for CO<sub>2</sub>/N<sub>2</sub> of the cross-linked nanocomposite membrane was enhanced. Recently, Peinemann et al.<sup>33</sup> reported the gas separation performance of nanostructured Pebax/polyethylene glycol dimethyl ether (PEG-DME) hybrid membranes. An 8-fold increase in CO<sub>2</sub> permeability was observed after the incorporation of 50 wt % PEG-DME in the copolymer, and the CO<sub>2</sub>/H<sub>2</sub> selectivity increased simultaneously from 9.1 to 14.9.

Through the formation of organic-inorganic hybrids, it is possible to capture the desirable attributes of the different components in a single composite, for example, the flexibility and processability of polymers, and the mechanical strength and thermal stability of the fillers, and possibly to discover new synergistic properties.<sup>34,35</sup> Since Pebax-1657 is a promising membrane material with a particular high selectivity for polarizable/nonpolar gas separation,<sup>30</sup> and doping Pebax-1657 with different fillers may further improve its gas separation properties,<sup>32,33</sup> we researched Pebax-1657 nanocomposite membranes incorporated with silica nanoparticles, PS colloids, and CNTs for gas separation in this paper. The effects of filler type, structure, and content to the CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separation performance of the nanocomposite membranes were studied and discussed preliminarily. Nanocomposite membranes with improved mechanical strength and gas separation performance were obtained using CNTs as the nanofiller.

## EXPERIMENTAL

### Materials

Styrene (St), methyl methacrylate (MMA), and acrylic acid (AA) were distilled before use. Sodium dodecyl sulfate (SDS) was chemical grade reagent and purified by recrystallization in ethanol before use. Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) were chemical grade reagent, and used as received. Silica nanopowder (SiO<sub>2</sub>, 10 nm in diameter) was purchased from Aldrich, and used as received. SWNT (HiPco<sup>®</sup>, >88%, 0.1–1 μm in length and 0.8–1.2 nm in diameter) and MWNT (>90%, 0.5–500 μm in length and 40–60 nm in diameter) were purchased from Unidym Inc. and Aldrich, respectively. Both of the CNTs were further purified by centrifuge to remove catalyst residues prior to use. Pebax-1657 (formerly sold under the trade name PEBAX-4011, comprise 60 wt % of PEO and 40 wt % PA-6) were provided by Arkema Inc., and used as received.

### Synthesis of Monodisperse PS Colloids

The monodisperse PS colloids with 190 nm diameter were synthesized by emulsion polymerization, a typical sample was prepared as follows: A 120 mL portion of aqueous solution (A)

containing (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.4 g), NH<sub>4</sub>HCO<sub>3</sub> (0.8 g), and SDS (0.08 g) in a funnel and 25 mL of monomer mixture (B) consisting of St/MMA/AA (90 : 5 : 5 v/v/v) in another funnel were added at the same time into a 250 mL flask, the mixture was stirred at 70°C in a N<sub>2</sub> atmosphere for 5 h to obtain a homogeneous latex with a particle diameter of 190 nm, and the latex particles were almost monodisperse with a polydispersity of 0.002.

### Membrane Preparation

Membranes of Pebax were cast onto glass plates at 25°C from their solutions of formic acid. The preparation of polymer/filler nanocomposite membranes is as follows: 0.6 g of Pebax was dissolved in 8 mL of formic acid with stirring in a beaker. Fillers (silica, PS colloid, SWNT, or MWNT) were added slowly into the polymer solution at 3.1, 5.3, 7.5, 11.1, and 33.3 wt % of the polymer, respectively. The mixture was vigorously stirred at a rotation speed of 1150 rpm for 15 min in order for the fillers to be dispersed uniformly in the polymer matrix. The mixture was then cast onto a clean and dry glass plate at 25°C. After the solvent was evaporated, the resulting membrane was peeled off and stored in a desiccator for testing. The thickness of the membranes was about 50–90 μm.

### Characterizations

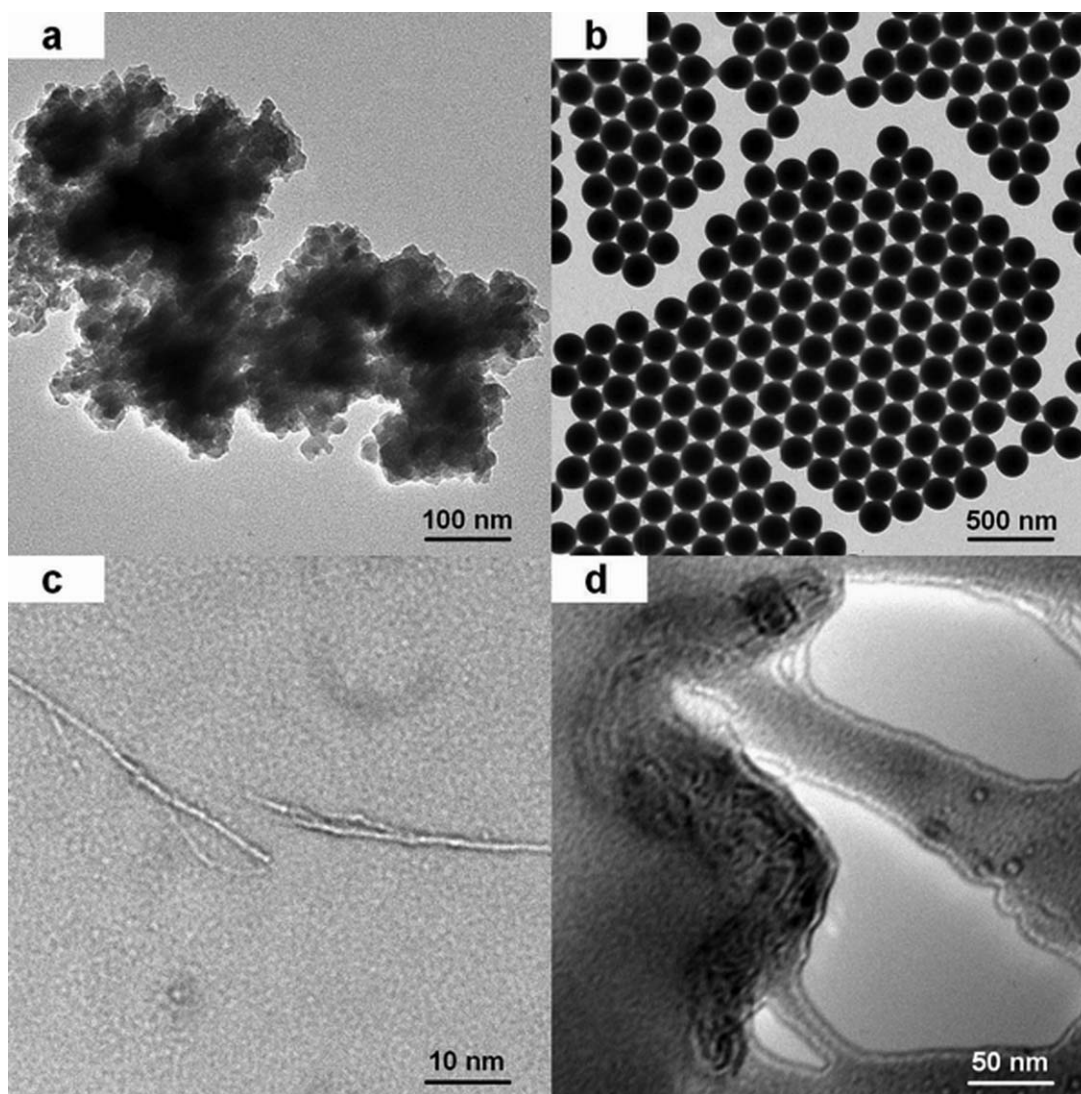
Transmission electron microscope (TEM, Hitachi H-7000) was used to observe the morphology of different fillers. Size and polydispersity of the fillers in formic acid were determined using a Malvern Zeta Sizer instrument. Scanning electron microscope (SEM, JEOL JSM-5800LV) was used to observe the surface morphology of the obtained membranes. Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of the membranes were determined by a differential scanning calorimeter (DSC, TA Instruments QP10) with a heating rate of 20°C/min. Mechanical property tests were carried out in a NanoBio-nix tensile tester (Systems, Oak Ridge, TN) at 25°C at a tensile speed of 5 cm/min. The reported membrane tensile modulus was an average of the results of five tests for each membrane.

### Gas Separation Performance Test

Pure-gas permeation tests were performed at 21°C and 33-psig feed upstream pressure using the constant-volume, variable-pressure technique,<sup>36–38</sup> in which a specimen was held under vacuum until it was exposed to a gas at a specific pressure. The value of gas permeability measured was determined from

$$P = \frac{VL}{ART\Delta P} \left[ \left( \frac{dp}{dt} \right)_{ss} - \left( \frac{dp}{dt} \right)_{leak} \right] \quad (1)$$

where  $P$  is the permeability [ $\text{cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cm Hg}$ ],  $V$  is the downstream volume ( $\text{cm}^3$ ),  $L$  is the membrane thickness (cm),  $A$  is the membrane area ( $\text{cm}^2$ ),  $R$  is the gas constant [ $= 0.278 \text{ cm Hg cm}^3/\text{cm}^3(\text{STP}) \text{ K}$ ],  $T$  is the absolute temperature (K),  $\Delta P$  is the transmembrane pressure difference ( $= p_2 - p_1$ , where  $p_2$  and  $p_1$  are the upstream and downstream pressures (cm Hg), respectively), and  $(dp/dt)_{ss}$  and  $(dp/dt)_{leak}$  are the steady-state rates of pressure rise (cm Hg/s) in the downstream volume at a fixed upstream pressure and under vacuum, respectively.<sup>18,39</sup> The diffusivity ( $D$ ) was determined from



**Figure 1.** TEM images of the fillers: (a) silica, (b) PS colloid, (c) SWNT, and (d) MWNT.

$$D = L^2 / 6\theta \quad (2)$$

where  $\theta$  is the time lag when a steady  $dp/dt$  rate is obtained on the downstream side in the permeation tests.<sup>38</sup> The solubility ( $S$ ) was determined from

$$S = P/D \quad (3)$$

and the permselectivity ( $\alpha$ ) was determined from

$$\alpha = P_A/P_B \quad (4)$$

where  $P_A$  and  $P_B$  are the permeabilities of pure gases A and B, respectively.

## RESULTS AND DISCUSSION

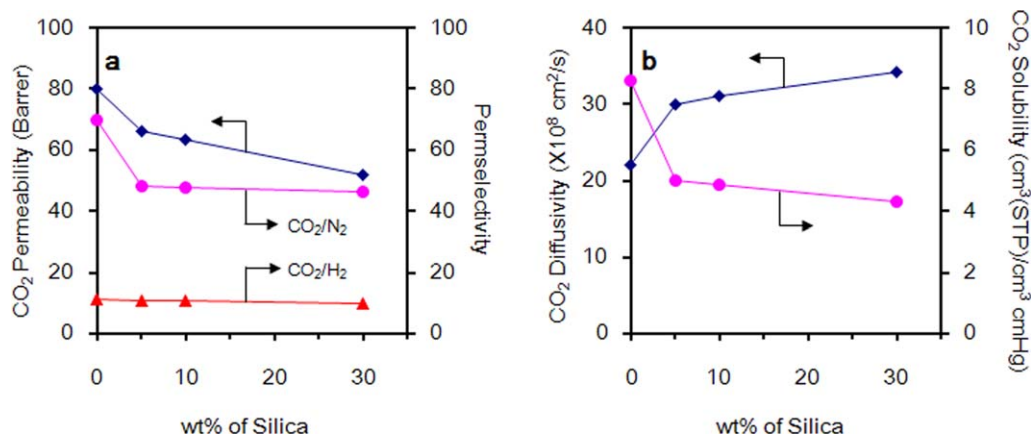
### Fillers

The TEM images of the fillers used in this study are depicted in Figure 1. The size and polydispersity data of the fillers in formic acid measured by Malvern Zeta Sizer instrument are listed in Table I. The 10 nm silica [Figure 1 (a)] nanoparticles have a strong tendency to aggregate, which is normal phenomenon in

nano-materials whereby their surface energy is minimized. Even in the casting solvent, the 10 nm silica nanoparticles also have a strong tendency to aggregate with a measured size value of 836 nm based on dynamic light scattering technique (Table I). The 190 nm PS colloids [Figure 1 (b)] are almost monodisperse. In the casting solvent, the PS colloids have a very weak tendency to aggregate with a measured size value of 204 nm and a

**Table I.** Size and Polydispersity of the Fillers in Formic Acid Measured by Malvern Zeta Sizer Instrument Based on Dynamic Light Scattering Technique

| Sample            | Size (nm) | Polydispersity |
|-------------------|-----------|----------------|
| 10 nm Silica      | 836       | 0.399          |
| 190 nm PS colloid | 204       | 0.002          |
| 1 nm SWNT         | 571       | 0.926          |
| 50 nm MWNT        | 987       | 0.983          |



**Figure 2.** Gas separation performance of Pebax-1657/silica nanocomposite membranes as a function of silica concentration: (a) permeability and permselectivity and (b) diffusivity and solubility (test conditions: 33 psig feed pressure at 21°C). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

polydispersity of 0.002 (Table I). The SWNTs [Figure 1 (c)] have an average diameter about 1 nm, while the MWNTs [Figure 1 (d)] have an average diameter about 50 nm. In the casting solvent, the measured size values of 571 nm for SWNTs, 987 nm for MWNTs are found with high polydispersity readings (Table I), which means the CNTs also have a strong tendency to aggregate.

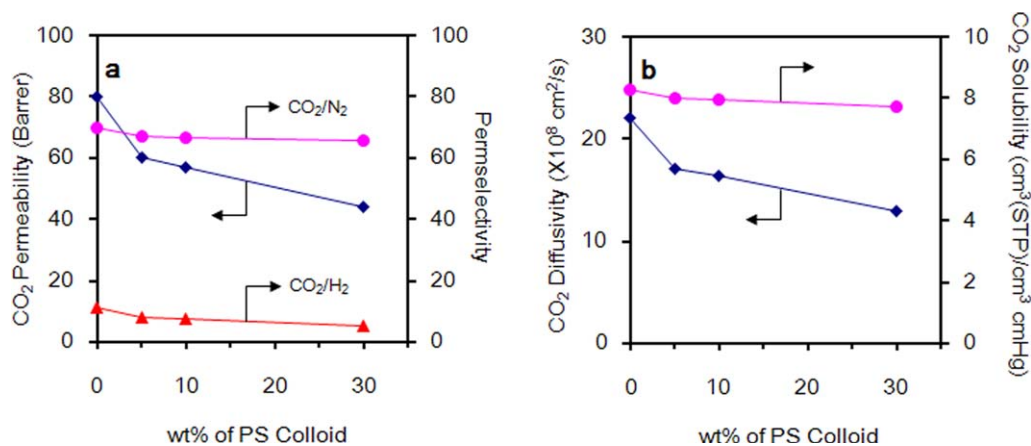
#### Pebax/Silica Nanocomposite Membranes

The permeability and selectivity (permselectivity) of the Pebax-1657/silica nanocomposite membranes, as a function of silica concentration, are summarized in Figure 2(a). The pure Pebax-1657 membrane has a  $P_{\text{CO}_2}$  of 80 Barrer. The CO<sub>2</sub> permeability of the silica doped Pebax-1657 membranes decreases with increasing the silica concentration. The  $P_{\text{CO}_2}$  of the Pebax-1657/silica membrane reduces to 52 Barrer at 30 wt % silica. The pure Pebax-1657 membrane has  $\alpha_{\text{CO}_2/\text{N}_2}$  of 70 and  $\alpha_{\text{CO}_2/\text{H}_2}$  of 11. The CO<sub>2</sub> selectivity over N<sub>2</sub> or H<sub>2</sub> of the silica doped Pebax-1657 membranes also decreases with increasing the silica concentration. The  $\alpha_{\text{CO}_2/\text{N}_2}$  and  $\alpha_{\text{CO}_2/\text{H}_2}$  of the Pebax-1657/silica membrane reduce to 46 and 9.6, respectively, at 30 wt %

silica. Further analysis [Figure 2 (b)] suggested that addition of silica significantly decreases the CO<sub>2</sub> solubility in the membranes which is probably due to the loss of polymer volume available for sorption, although addition of silica increases the CO<sub>2</sub> diffusivity to some extent for disturbing the polymer chain packing.<sup>40,41</sup> Since permeability is the product of diffusivity and solubility, the decrease in CO<sub>2</sub> permeability is attributed to silica-decreased CO<sub>2</sub> solubility. Lee et al.<sup>42</sup> reported that the Pebax-1657 membrane containing 27 wt % of silica had a  $P_{\text{CO}_2}$  of 277 Barrer and a  $\alpha_{\text{CO}_2/\text{N}_2}$  of 79, which are much higher than the data reported in Figure 2 (a). The main reason for the difference is that they make the Pebax-1657/silica hybrid membranes using in situ sol-gel reactions, and the silica nanoparticles generated by this method are smaller in size and dispersed well in the polymer matrix.

#### Pebax/PS Colloid Nanocomposite Membranes

The permeability and selectivity of the Pebax-1657/PS colloid nanocomposite membranes, as a function of silica concentration, are summarized in Figure 3(a). The CO<sub>2</sub> permeability of the PS



**Figure 3.** Gas separation performance of Pebax-1657/PS colloid nanocomposite membranes as a function of silica concentration: (a) permeability and permselectivity and (b) diffusivity and solubility (test conditions: 33 psig feed pressure at 21°C). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Mechanical Properties of Pebax-1657 Based Nanocomposite Membranes

| Polymers            | Elongation (%) | Tensile modulus (MPa) |
|---------------------|----------------|-----------------------|
| Pebax               | 172            | 80                    |
| Pebax/5% SWNT       | 64             | 114                   |
| Pebax/5% MWNT       | 85             | 99                    |
| Pebax/5% Silica     | 91             | 88                    |
| Pebax/5% PS colloid | 102            | 84                    |

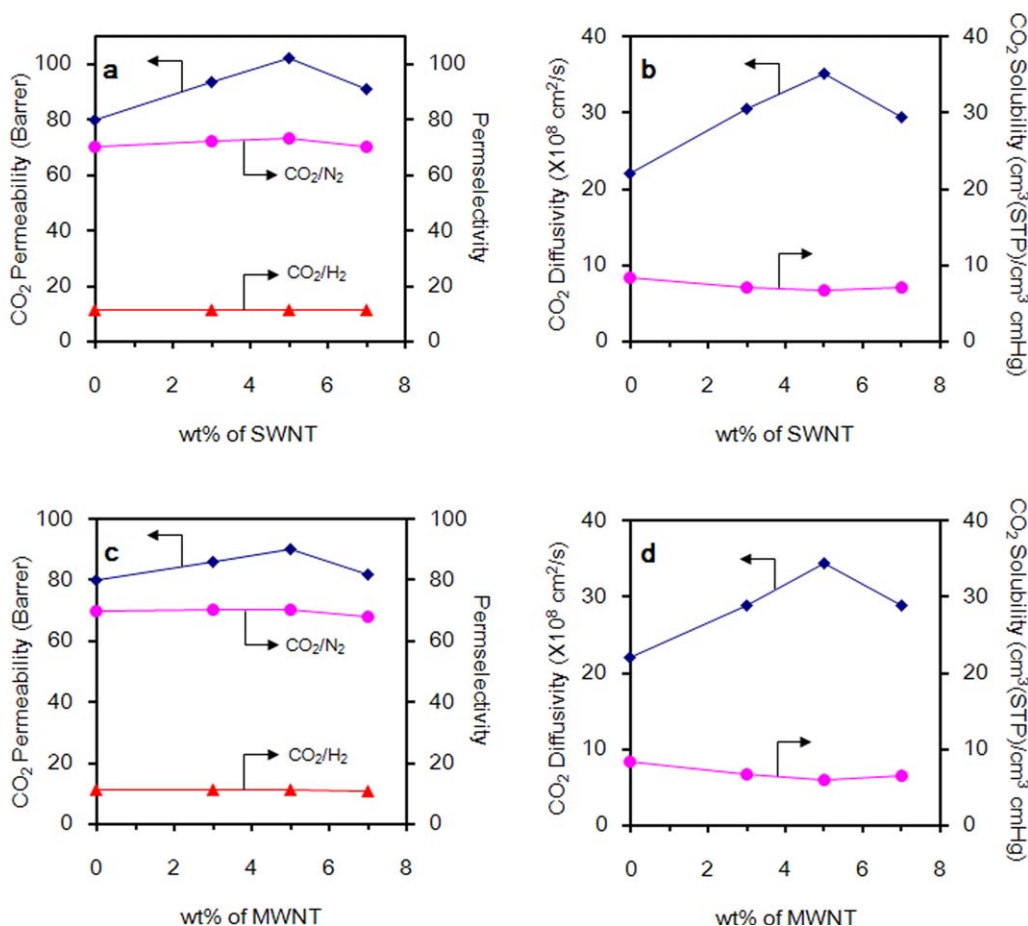
colloid doped Pebax-1657 membranes decreases with increasing the PS colloid concentration. The  $P_{CO_2}$  of the Pebax-1657/PS colloid membrane reduced to 44 Barrer at 30 wt % PS colloids. The  $CO_2$  selectivity over  $N_2$  or  $H_2$  of the PS colloid doped Pebax-1657 membranes also decreases with increasing the PS colloid concentration. The  $\alpha_{CO_2/N_2}$  and  $\alpha_{CO_2/H_2}$  of the Pebax-1657/PS colloid membranes reduce to 66 and 5.4, respectively, at 30 wt % PS colloids. Further analysis [Figure 3 (b)] suggested that addition of PS colloid significantly decreases the  $CO_2$  diffusivity in the membranes which is probably due to the increase of the penetrant diffusion pathway length, and addition of PS colloid also

decreases the  $CO_2$  solubility to some extent for loss of Pebax volume available for sorption.<sup>40,41</sup>

### Pebax/CNT Nanocomposite Membranes

The CNT-containing Pebax-1657 nanocomposite membranes are fabricated by mixing the polymers with 3, 5, and 7 wt % of SWNT (o.d.: 0.8–1.2 nm, length: 0.1–1  $\mu m$ ) or MWNT (o.d.: 40–60 nm, length: 0.5–500  $\mu m$ ) in formic acid solutions and casting onto glass plates. The membranes have very good mechanical properties when the CNT content is less than 7 wt %. In Table II, at 5 wt % SWNTs and MWNTs, the tensile modulus of Pebax-1657 increases about 43 and 24%, respectively. The tensile modulus of Pebax-1657/CNT nanocomposites is higher than that of Pebax-1657/silica or Pebax-1657/PS colloid nanocomposites at the same nanofiller content.

The gas separation properties of the Pebax-1657/SWNT and Pebax-1657/MWNT nanocomposite membranes, as a function of CNT concentration, are summarized in Figure 4 (a) and (c), respectively. The  $CO_2$  permeability of both the SWNT- and MWNT-doped Pebax-1657 membranes initially increases with increasing the CNT concentration. The  $P_{CO_2}$  of the Pebax/CNT nanocomposite membrane reached 102 Barrer at a 5 wt % SWNTs, and 90 Barrer at 5 wt % MWNTs. The addition of



**Figure 4.** Gas separation performance of Pebax-1657/SWNT (a and b) and Pebax-1657/MWNT (c and d) nanocomposite membranes as a function of CNT concentration (test conditions: 33 psig feed pressure at 21°C). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**Table III.** Thermal Properties of Pebax-1657 Based Nanocomposite Membranes

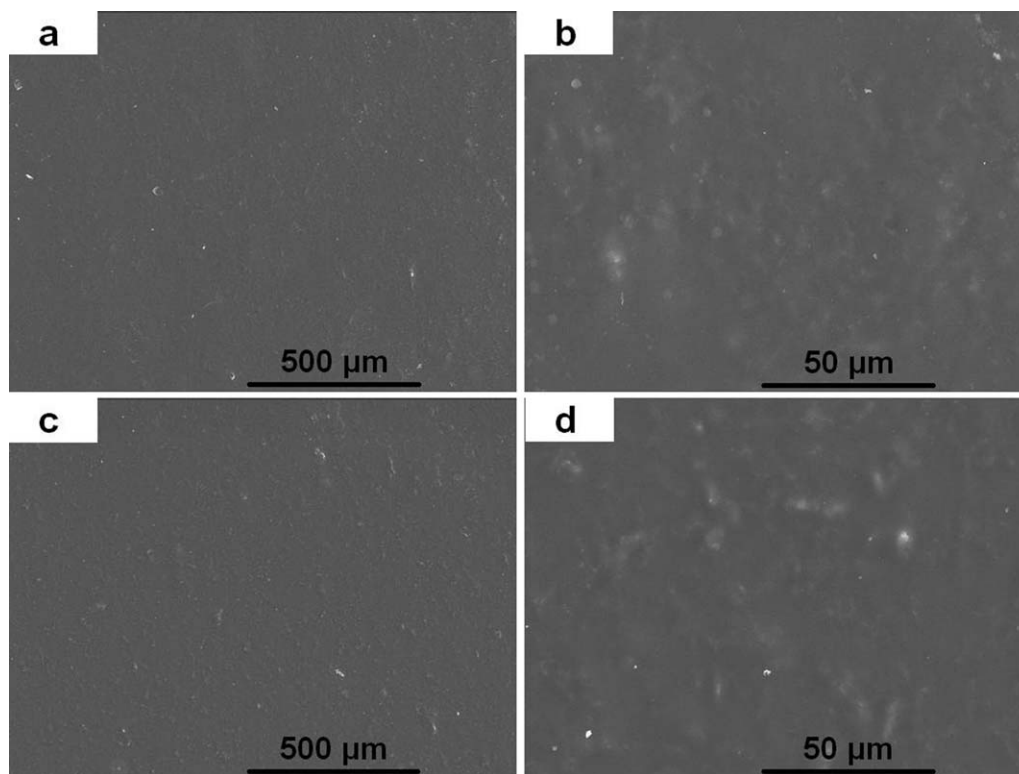
| Polymers            | $T_g$ (°C) | $T_m$ -PEO (°C) | $T_m$ -PA (°C) |
|---------------------|------------|-----------------|----------------|
| Pebax               | -53        | 7               | 208            |
| Pebax/3% SWNT       | -52        | 6               | 209            |
| Pebax/5% SWNT       | -51        | 6               | 208            |
| Pebax/7% SWNT       | -48        | 7               | 207            |
| Pebax/5% MWNT       | -52        | 6               | 208            |
| Pebax/5% Silica     | -51        | 7               | 207            |
| Pebax/5% PS colloid | -52        | 7               | 207            |

CNT has little impact on the selectivity. This suggests that adding CNT improves rather than deteriorates the gas separation properties of the membranes, making it feasible to use CNT to enhance the membrane's mechanical strength. Further analysis [Figure 4 (b,d)] suggested that CNT does not significantly affect the CO<sub>2</sub> solubility in the membranes, but substantially increases the CO<sub>2</sub> diffusivity. The increase in the permeability is attributed to CNT-increased gas diffusivity. At CNT concentrations higher than 5 wt %, both CO<sub>2</sub> permeability and selectivity of their nanocomposite membranes decrease. Figure 4 also shows that at the same CNT concentration (5 wt %), the CO<sub>2</sub> permeability of the Pebax/SWNT membrane is higher than that of Pebax/MWNT. So SWNT is more effective than the MWNT in enhancing CO<sub>2</sub> permeability of the membranes. The possible reason for this phenomenon is: MWNT has multi-walled

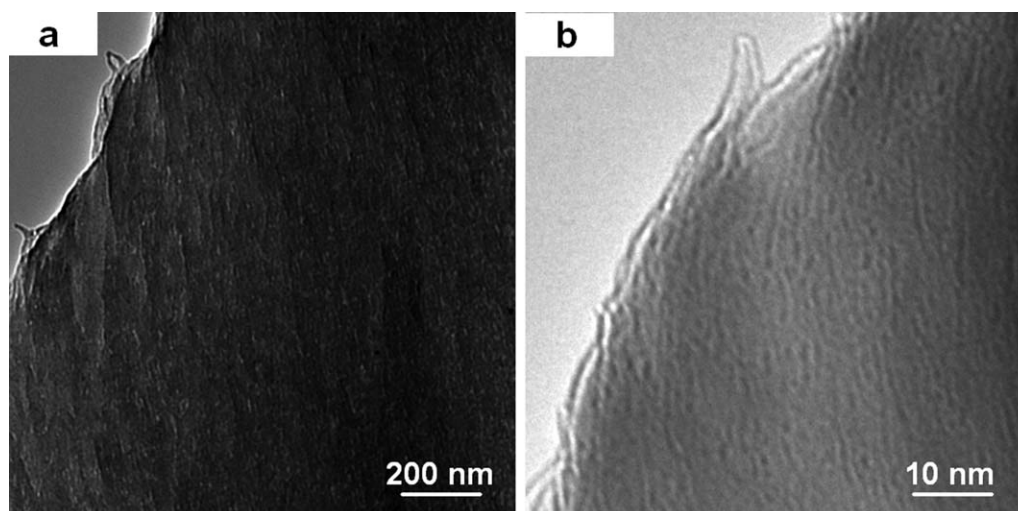
**Table IV.** Gas Separation Performance of Pebax-1657/5 wt % SWNT Membranes Fabricated from Different Polymer Concentrations

| Pebax/5 wt % SWNT nanocomposite membranes | $P_{CO_2}$ (Barrer) | $P_{N_2}$ (Barrer) | $P_{H_2}$ (Barrer) | $\alpha_{CO_2/N_2}$ | $\alpha_{CO_2/H_2}$ |
|---|---------------------|--------------------|--------------------|---------------------|---------------------|
| From 5.7 wt % polymer concentration       | 102                 | 1.40               | 9.04               | 73.0                | 11.3                |
| From 17 wt % polymer concentration        | 105                 | 1.45               | 9.11               | 72.4                | 11.5                |

structures, which can be seen as a special aggregation phase of SWNT, and the aggregation of nanofillers usually hurts the gas separation performance of nanocomposite membranes. Recently, Sridhar et al.<sup>32</sup> reported that the Pebax-1657/MWNT nanocomposite membranes containing 5 wt % of MWNT had a  $P_{CO_2}$  of 262.15 Barrer and a  $\alpha_{CO_2/N_2}$  of 58.5, which are different from the data reported in Figure 4 (c). The possible reason for the difference lies in two aspects: on the one hand, the diameter and length of MWNT fillers (diameter 10–20 nm, length 5–15  $\mu$ m) used in their research are different from ours (diameter 40–60 nm, length 0.5–500  $\mu$ m); on the other hand, the feed pressure and testing temperature of their membranes (1 MPa and 30°C) are both higher than ours (33 psig and 21°C).



**Figure 5.** SEM surface morphologies of Pebax-1657/5 wt % SWNT membranes fabricated from 5.7 wt % (a and b) and 17 wt % (c and d) polymer concentrations.



**Figure 6.** TEM images of Pebax-1657/5 wt % SWNT membranes: (a) low resolution image to show black (aggregation) and white (dispersion) regions and (b) high resolution image of the white region of a.

In Table III, the  $T_g$  value of 7 wt % SWNT composited Pebax-1657 membrane is  $-48^\circ\text{C}$ . It is much higher than that of Pebax-1657 ( $-53^\circ\text{C}$ ), which shows that the polymer chain suffers rigidification at high SWNT concentration, and it may account for the drop in  $\text{CO}_2$  diffusivity at high filler concentration. Compared with  $T_g$ , the effect of 7 wt % SWNT to the  $T_m$  values of Pebax-1657 is not significant. Adding CNT, silica, or PS colloid nanofillers to Pebax-1657 matrix increases  $T_g$  of the samples. Pebax-1657 consists of PA and PEO crystalline phases.<sup>25,33,42</sup> Adding 5 wt % CNTs decreases the  $T_m$ -PEO, while does not seem to influence the  $T_m$ -PA, which indicates the PEO crystalline phase is greatly modified by the incorporation of CNTs in Pebax-1657. Therefore, the increase of gas permeability in Pebax/CNT nanocomposites should mainly attribute to the contribution of the permeability of the modified PEO phases.

Heterogeneity, which is defined as fillers separating out from the membrane matrix due to the gravity or incompatibility and forming separate filler phases or layers during the formation of the nanocomposite membranes, may occur in polymer-inorganic nanocomposite membranes. Heterogeneity may deteriorate the gas separation performance of the membranes. To test the possible heterogeneity of CNTs in the membranes, two Pebax-1657/5 wt % SWNT nanocomposite membranes are cast from 5.7 wt % and 17 wt % polymer solutions at the same filler-to-polymer ratio. The viscosity of the 17 wt % polymer solution is much higher than that of the 5.7 wt % solution and thus will minimize or inhibit heterogeneity of the CNTs in the membranes. The results shown in Table IV and Figure 5 clearly indicate that the gas separation performances and surface morphologies of the two membranes have no difference, indicating that CNTs do not undergo heterogeneity during the membrane casting.

The TEM images shown in Figure 6 illustrate that in the Pebax-1657/SWNT membranes, some CNTs aggregate (black parts) and some disperse (white parts). Mechanical mixing could not completely eliminate the aggregations, especially for the Pebax-1657 matrix with binary phases of PEO and PA.

### Mechanism of CNT-Enhanced Gas Permeability

Adding impermeable nanoparticles to a polymer is typically expected to reduce the gas permeability.<sup>43</sup> Maxwell's model, developed to analyze the steady-state dielectric properties of a diluted suspension of spheres,<sup>44</sup> is often used to model permeability in membranes filled with roughly spherical impermeable particles [eq. (5)].<sup>45</sup>

$$P_c = P_p(1 - \Phi_f) / (1 + 0.5\Phi_f) \quad (5)$$

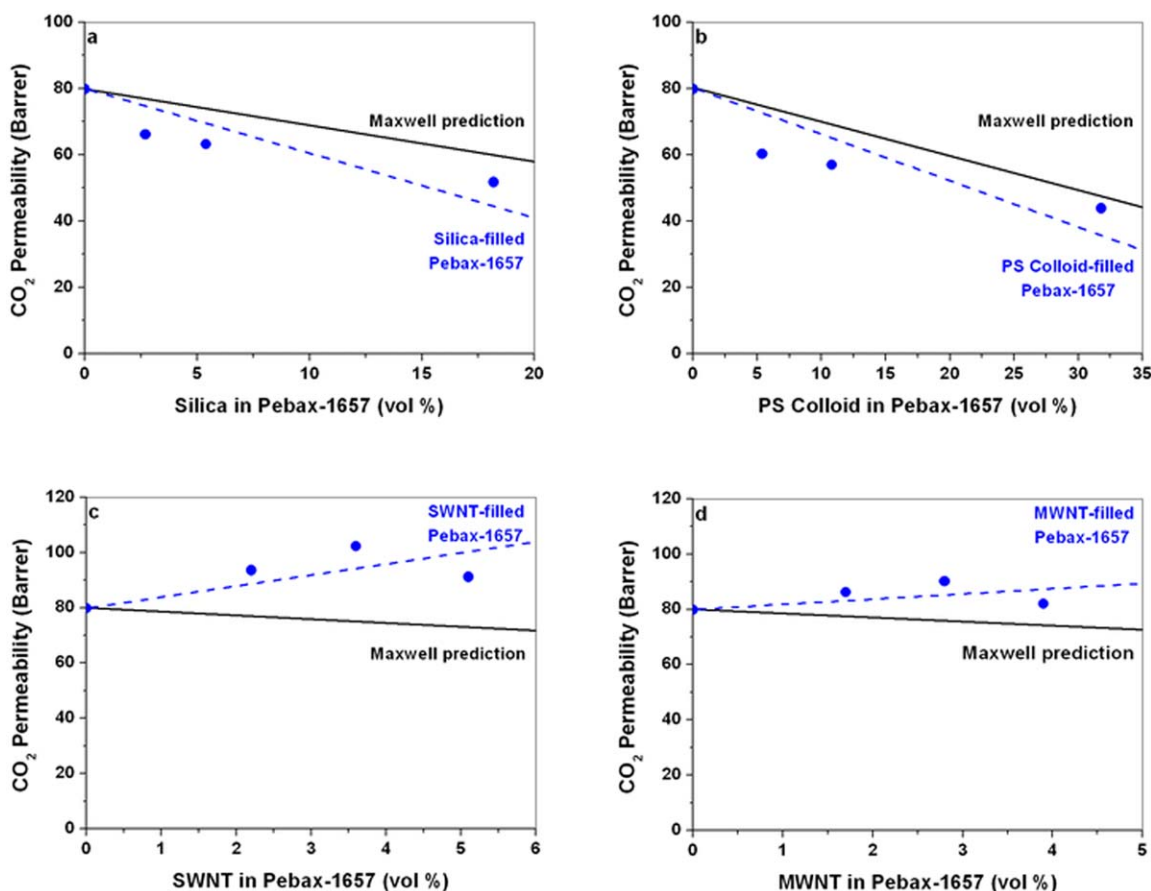
where  $P_c$  and  $P_p$  are the permeability of the nanocomposite and the pure polymer matrix, respectively, and  $\Phi_f$  is the volume fraction of the filler.

As provided by the vendor, the densities of Pebax-1657, silica nanoparticles, SWNTs, and MWNTs are 1.14, 2.2, 1.6, and 2.1  $\text{g}/\text{cm}^3$ , respectively. The measured density of PS colloids is 1.05  $\text{g}/\text{cm}^3$ . Therefore, the weight percents of the different fillers in the Pebax-1657 nanocomposite membranes are converted into volume percents and listed as Table V.

In Figure 7, Maxwellian-like effects are observed in the silica- and PS colloid-filled Pebax-1657 membranes, probably because the silica nanoparticles is impermeable and the PS colloids have ideal sphere shape, and they both satisfy at least one of the conditions of the Maxwell's model; while non-Maxwellian effects are observed in the SWNT- and MWNT-filled Pebax-1657 membranes, probably because the CNTs are permeable inside

**Table V.** Conversion Table from Weight Percent to Volume Percent of Different Fillers in Pebax-1657 Nanocomposite Membranes

| Filler     | wt %  | 3   | 5   | 7   | 10   | 30   |
|------------|-------|-----|-----|-----|------|------|
| Silica     | vol % | 1.6 | 2.7 | 3.8 | 5.4  | 18.2 |
| PS colloid | vol % | 3.2 | 5.4 | 7.6 | 10.8 | 31.8 |
| SWNT       | vol % | 2.2 | 3.6 | 5.1 | 7.3  | 23.4 |
| MWNT       | vol % | 1.7 | 2.8 | 3.9 | 5.7  | 18.9 |



**Figure 7.** CO<sub>2</sub> permeability of (a) Pebax-1657/silica, (b) Pebax-1657/PS colloid, (c) Pebax-1657/SWNT, and (d) Pebax-1657/MWNT membranes as a function of filler content in volume at 21°C and 33 psig feed pressure. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

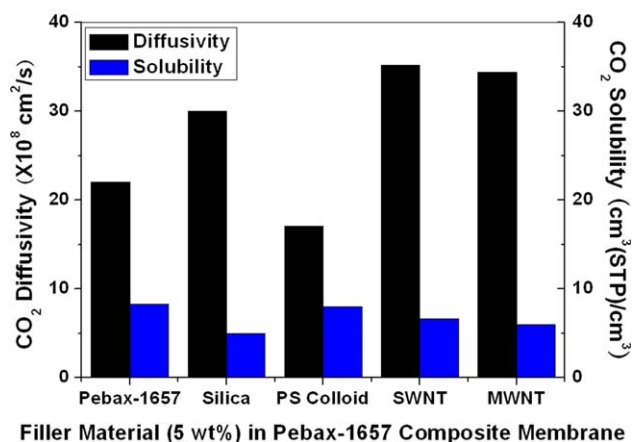
the hollow structures and have the special tube-like shapes, and they do not meet any conditions of the Maxwell's model.

Figure 8 shows the CO<sub>2</sub> diffusivity and solubility in the Pebax-1657 nanocomposite membranes containing 5 wt % fillers of different materials. At the same filler concentration, the CO<sub>2</sub> diffusivities of the Pebax-1657/SWNT and Pebax-1657/MWNT membranes are higher than those of Pebax-1657/PS colloid and Pebax-1657/silica membranes. For the CNT does not significantly affect the CO<sub>2</sub> solubility in the membranes, the enhanced gas permeability is attributed to CNT-increased gas diffusivity, which should come from two possible aspects: on the one hand, as nanofillers with special shapes, CNTs can insert into polymer chains and generate more free volumes for gas diffusion by disturbing the polymer chain packing; on the other hand, because CNTs possess hollow structures, gas molecules might transport inside the nanotubes and have additional mass transfer routes, which increase the apparent diffusivity of gas molecules.

#### Gas Separation Performance of Pebax-1657/CNT Nanocomposite Membranes

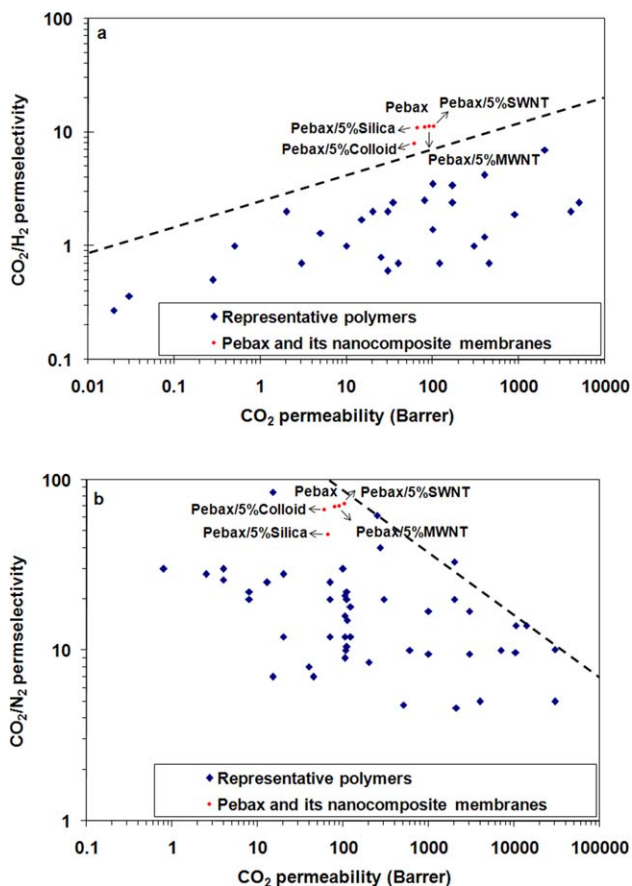
In Figure 9 (a), the CO<sub>2</sub> permeability and CO<sub>2</sub>/H<sub>2</sub> selectivity of Pebax-1657/CNT membranes are not only above a upper bound proposed by Freeman et al.,<sup>46</sup> but also above those of pure Pebax-1657 membranes, which indicates that the Pebax-1657/

CNT nanocomposite membranes may be useful for CO<sub>2</sub>/H<sub>2</sub> separation. In Figure 8 (b), the CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity of Pebax-1657/CNT membranes are close to the updated Robeson's upper bound, which is based on literature data taken mostly at 35°C.<sup>47</sup>



**Figure 8.** Comparison of CO<sub>2</sub> diffusivity and solubility in the Pebax-1657 nanocomposite membranes containing 5 wt % fillers of different materials at 21°C and 33 psig feed pressure. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 9.** CO<sub>2</sub>/H<sub>2</sub> (a) and CO<sub>2</sub>/N<sub>2</sub> (b) separation performances of Pebax-1657 and its nanocomposite membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSIONS

Pebax-1657 nanocomposite membranes incorporated with silica nanoparticles, PS colloids, and CNTs were fabricated successfully for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separation. Silica- and PS colloid-impregnated Pebax-1657 membranes had decreased CO<sub>2</sub> permeability and selectivity over N<sub>2</sub> or H<sub>2</sub> compared to the pure Pebax-1657 membrane, while CNT-impregnated Pebax-1657 membranes had increased CO<sub>2</sub> permeability but similar CO<sub>2</sub>/N<sub>2</sub> or CO<sub>2</sub>/H<sub>2</sub> selectivity compared to the pure polymer membrane. At 5 wt % SWNTs and MWNTs, the tensile modulus of Pebax-1657 increased by 43 and 24%, and the CO<sub>2</sub> permeability of the membrane also increased by 28 and 13%, respectively. The CO<sub>2</sub> permeability increased with increasing CNT content and reached a maximum at 5 wt % CNTs. The CNT-enhanced gas permeability was attributed to the increase in gas diffusivity, which came from the increase in free volume and gas transportation inside the nanotubes. Thus, it is feasible to add CNTs to Pebax-1657 membranes for improved mechanical strength and gas separation performance.

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## REFERENCES

- Koros, W. J.; Mahajan, R. J. *Membr. Sci.* **2000**, *175*, 181.
- Freeman, B. D. *Macromolecules* **2009**, *32*, 375.
- Yamada, Y.; Suzuki, T. *J. Appl. Polym. Sci.* **2013**, *127*, 316.
- Noble, R.D. *Ind. Eng. Chem. Res.* **2005**, *44*, 2887.
- Yu, X.; Zhang, Z.; Rao, H.; Liu, F. *J. Appl. Polym. Sci.* doi: 10.1002/app.38350.
- Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.
- Li, W.; Zhang, X.; Xing, W.; Jin, W.; Xu, N. *Ind. Eng. Chem. Res.* **2010**, *49*, 11244.
- Ge, L.; Zhu, Z.; Li, F.; Liu, S.; Wang, L.; Tang, X.; Rudolph, V. *J. Phys. Chem. C* **2011**, *115*, 6661.
- Bernardo, P.; Jansen, J. C.; Bazzarelli, F.; Tasselli, F.; Fuoco, A.; Friess, K.; Izak, P.; Jarmarova, V.; Kacirkova, M.; Clarizia, G. *Sep. Purif. Technol.* **2012**, *97*, 73.
- Tsai, M. H.; Huang S. L.; Chiang P. C.; Chen C. J. *J. Appl. Polym. Sci.* **2007**, *106*, 3185.
- Cong, H.; Hu X.; Radosz M.; Shen Y. *Ind. Eng. Chem. Res.* **2007**, *46*, 2567.
- Cong, H.; Zhang J.; Radosz M.; Shen Y. *J. Membr. Sci.* **2007**, *294*, 178.
- Ismail, A. F.; Rahim R. A.; Rahman W. A. *Sep. Purif. Technol.* **2008**, *63*, 200.
- Tena, A.; Fernandez L.; Sanchez M.; Palacio L.; Lozano A. E.; Hernandez A.; Pradanos P. *Chem. Eng. Sci.* **2010**, *65*, 2227.
- Cai, Y.; Wang Z.; Yi C.; Bai Y.; Wang J.; Wang S. *J. Membr. Sci.* **2008**, *310*, 184.
- Cong, H.; Yu B.; Tang J.; Zhao X. S. *J. Polym. Res.* **2012**, *19*, 9761.
- Yave, W.; Car, A.; Peinemann, K. V.; Shaikh, M. Q.; Ratzke, K.; Faupel, F. *J. Membr. Sci.* **2009**, *339*, 177.
- Cong, H.; Yu, B. *Ind. Eng. Chem. Res.* **2010**, *49*, 9363.
- Zhu, J.; Zhou, J.; Zhang, H.; Chu, R. *J. Polym. Res.* **2011**, *18*, 2011.
- Ren, X.; Ren, J.; Deng, M. *Sep. Purif. Technol.* **2012**, *89*, 1.
- Tocci, E.; Gugliuzza, A.; Lorenzo, L. D.; Macchione, M.; Luca, G. D.; Drioli, E. *J. Membr. Sci.* **2008**, *323*, 316.
- Potreck, J.; Nijmeijer, K.; Kosinski, T.; Wessling, M. *J. Membr. Sci.* **2009**, *338*, 11.
- Car, A.; Stropnik, C.; Yave, W.; Peinemann, K. V. *Sep. Purif. Technol.* **2008**, *62*, 110.

24. Seymour, R. B.; Kirshenbaum, G. S. *High Performance Polymers: Their Origins and Development*; Elsevier: New York, **1986**.
25. Car, A.; Stropnik, C.; Yave, W.; Peinemann, K. V. *J. Membr. Sci.* **2008**, *307*, 88.
26. Ben Hamouda, S.; Langevin, D.; Roudesli, S. *Phys. Proc.* **2009**, *2*, 723.
27. Sridhar, S.; Aminabhavi, T. M.; Mayor, S. J.; Ramakrishna, M. *Ind. Eng. Chem. Res.* **2007**, *46*, 8144.
28. Wang, Y.; Ren, J.; Degn, M. *Sep. Purif. Technol.* **2011**, *77*, 46.
29. Bondar, V.; Freeman, B. D.; Pinnau, I. *J. Polym. Sci. B* **1999**, *372*, 463.
30. Kim, J. H.; Ha, S. Y.; Lee, Y. M. *J. Membr. Sci.* **2001**, *190*, 179.
31. Zoppi, R. A.; Neves, S.; Nunes, S. P. *Polymer* **2000**, *41*, 5461.
32. Surya Murali, R.; Sridhar, S.; Sankarshana, T.; Ravikumar, Y. V. *Ind. Eng. Chem. Res.* **2010**, *49*, 6530.
33. Yave, W.; Car, A.; Peinemann, K. V. *J. Membr. Sci.* **2010**, *350*, 124.
34. Freeman, B. D.; Pinnau, I. *Polymer Membranes for Gas and Vapor Separation: Chemistry and Material Science*; American Chemical Society: Washington DC, **1999**.
35. Patel, N. P.; Miller, A. C.; Spontak, R. *J. Adv. Mater.* **2003**, *15*, 729.
36. Koros, W. J.; Chan, A. H.; Paul, D. R. *J. Membr. Sci.* **1977**, *2*, 165.
37. Fava, R. *Permeation, Diffusion and Sorption of Gases and Vapors*; Academic Press: New York, **1978**.
38. Lin, W. H.; Vora, R. H.; Chung, T. S. *J. Polym. Sci.* **2000**, *38*, 2703.
39. Cizchos, H.; Saito, T.; Smith, L. *Springer Handbook of Materials Measurement Methods*; Springer: New York, **2006**.
40. Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. *J. Chem. Mater.* **2003**, *15*, 109.
41. Freeman, B. D. *Novel Nanocomposite Membrane Structures for H<sub>2</sub> Separations, Final Technical Progress Report Prepared for the U. S. Department of Energy; DOE: Washington DC, 2005*.
42. Kim, J. H.; Lee, Y. M. *J. Membr. Sci.* **2001**, *193*, 209.
43. Barrer, R. M. *Diffusion in Polymers*; Academic Press: New York, **1968**.
44. Maxwell, C. *Treatise on Electricity and Magnetism*; Oxford University Press: London, **1873**.
45. Barrer, R.M.; Barrie, J. A.; Rogers, M. G. *J. Polym. Sci. A* **1963**, *1*, 2565.
46. Lin, H.; Wagner, E. V.; Freeman, B. D.; Toy, L. G.; Gupta, R. P. *Science* **2006**, *311*, 639.
47. Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390.