Concatenation of carbonaceous nanofillers for mixed matrix membrane development

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Abstract. Two different carbonaceous nanofillers, carbon nanofiber (CNF) and graphene oxide (GO) were synergistically incorporated into glassy poly (2,6-dimethyl-1,4-phenylene oxide) (PPO₅₉₆₈) polymer to synthesize a novel mixed matrix membrane (MMM) for CO₂/CH₄ separation. The combined effect of binary filler on the filler dispersion and gas separation performance of resultant membrane were analysed. The binary filler-based MMM rendered homogenous filler dispersion quality, as compared to single filler-based MMM. The CNF particles dispersed in between GO nanosheets, inhibited the restacking of GO whilst the strong steric effect imposed by GO nanosheets improved the dispersion of CNF particles in the polymer matrix. The optimum gas separation performance was recorded at 2 wt% CNF/3 wt% GO loading with ideal CO₂/CH₄ selectivity of 59.70 and CO₂ permeability of 62.32 Barrer at 3.5 bar feed pressure. The CNF particles with smooth wall and larger diameter allowed gases to diffuse through faster by creating a gas pathway and eventually improved the gas permeability. Meanwhile, GO nanosheets with surface hydroxyl and carboxyl groups facilitated the transport mechanism of CO₂ molecules, acted as a selective barrier and rendered high selectivity. Therefore, both permeability and selectivity of resultant membrane were enhanced.

1. Introduction

Mixed matrix membrane (MMM) is a heterogeneous membrane consisting of inorganic filler embedded in polymer matrix. It combines the desirable properties of both polymeric and inorganic material to form high performance gas separating membrane. Generally, the addition of inorganic fillers is expected to alter the transport properties of gases, modify the properties of the neighbour polymer phase and alter the packing, dynamics or conformation of polymer chain near its surface [1]. According to Ismail et.al., [2] the integration of inorganic fillers enhances the gas separation properties of polymer matrix via two ways. Firstly, the interaction between the polymer-filler particles disrupt the polymer chain packing, increases the polymer matrix free-volume and eventually increases the gas diffusion parameter. Thereafter, the functional groups attached on the filler surface interact with some gases and enhances the gas solubility parameter. Over the past decades, various inorganic particles have been incorporated in the polymer matrix to form MMM. Excessive works have been carried out especially with the conventional fillers including zeolites, silicas, metal oxides and carbon molecular sieves as they possess some unique and individualistic properties which contributed positively to the robust performance of resultant membrane [3]. Various modifications have been performed on the filler particles and the performance of resultant membrane were well documented. However, Goh et.al., [4] found that the development of MMMS using
these conventional fillers has reached its bottleneck whereby the performance of resultant membrane could not be further improved. Meanwhile, very few works have been reported on the utilization of alternative fillers in MMM fabrication, thus far. Alternative fillers are relatively new for gas separation membrane synthesis and its full potential is yet to be explored.

Besides, the recent practice of developing MMM using nano-sized inorganic filler is found to encounter severe agglomeration issues in polymer matrix due to their high specific surface area and strong intermolecular van der Waals interactions. Moreover, the addition of single filler was often insufficient to improve both permeability and selectivity of resultant membranes [5]. Therefore, in order to improve the filler dispersion properties and to enhance the gas separation efficiency, a new technique of combining two different fillers with distinct properties, morphologies, nature and dimension in the polymer matrix is proposed [6-10]. In this technique, two fillers are synergistically incorporated into a polymer matrix at different weight loading to engineer the performance of resultant MMM. The complementary interaction between the two fillers with distinct surface chemistry promote polymer-filler interaction, thereby reducing the possibilities of filler agglomeration, whilst retaining the native properties of the filler particles. On top of that, it is hypothesized that the addition of binary fillers could enhance both permeability and selectivity of MMM. One of these binary fillers could improve the gas permeability across the membrane while the other could enhance the selectivity. Therefore, this work focuses on the development of a novel MMM with enhanced filler dispersion and gas separation performance using two different alternative carbonaceous nanofillers, namely carbon nanofiber (CNF) and graphene oxide (GO). To the best of author’s knowledge, these filler combinations has not been attempted in gas separation membrane development.

2. Materials and Method

2.1. Material
Poly (2,6-dimethyl-1,4-phenylene oxide) (PPOdm) polymer powder and chloroform solvent with ≥ 99.5 purity were purchased from Sigma Aldrich. Carbon nanofiber (CNF, > 70% purity) and graphene oxide (GO, > 99% purity) with an average diameter of 200 nm and 500 nm, respectively were purchased from Suzhou Hengqiu Graphene Technology Co. Ltd, China. Carbon dioxide (CO₂) and methane (CH₄) gases with > 99.995% purity were supplied by Gas Walker, Malaysia.

2.2. Membrane fabrication
Five membranes with different filler loadings (Table 1) were synthesized via dry-phase inversion technique, as depicted in Figure 1. A specified amount of filler was ultra-sonicated for 30 min in chloroform to form well-dispersed homogenous suspension. Subsequently, 22 wt% of preheated polymer powder was added to the filler-solvent suspension gradually with continuous stirring for 24 h at 60°C. The dope solution was degassed for 4 h and allowed to stand at room temperature overnight. The solution was cast on a clean glass plate using a film applicator at a gap setting of 150 µm and allowed to dry at room temperature for the first 24 h, followed by drying by at 80°C for 72 h. For binary filler-based MMM, similar procedures were used in which CNF particles were sonicated for the first 30 min and further sonicated for another 30 min after the adding GO in the suspension. Meanwhile, pristine PPOdm membrane was fabricated via the same procedure without the addition of filler particles.

2.3. Characterization
Powder X-Ray Diffractometer (XRD, X’Pert³ Powder & Empyrean, PANalytical) was used to study the atomic arrangement of polymer chain upon the incorporation of filler particles. The analysis was carried out in the 2θ range of 5-90° with scanning speed of 10°/min. The spacing between two adjacent planes (d-spacing) was calculated using Bragg’s equation 1.0:
where $\lambda$ is the wavelength of CuKα radiation ($\lambda=0.1540$ nm), $d$ is the basal spacing and $\sin \theta$ is the scattering angle.

The surface and cross sectional morphology of membranes were analyzed using Variable Pressure Field Emission Scanning Electron Microscope (VP-FESEM, Zeiss SupraTM 55 VP) at an accelerating voltage of 15 kV. All membrane samples were sputter-coated with gold using Polaron Range SC 7640. For cross-sectional analysis, the membrane samples were cryofractured with liquid N₂ prior to scanning.

The dispersion and distribution properties of filler particles in the PPO_{dm} polymer matrix were further examined using Optical Microscope (OM, OLYMPUS Model BX53M) at 500 X magnification. For clearer visual inspection, the images were converted to binary images wherein for single filler-based MMM the filler particles were depicted in red, while for binary filler-based MMM, GO and CNF were portrayed in yellow and blue, respectively.

### 2.4. Gas permeation test

The gas permeation properties of resultant membrane were measured using an in-house gas permeation test rig at fixed feed pressure of 3.5 bar and room temperature. Membrane with an effective surface area of 1.77 cm² were dried for at least 1 h and secured on a metal plate of a flat sheet membrane module. The permeate flow rate across the membrane was measured using a soap bubble flow meter after the system reached equilibrium. Five measurements were taken for each sample and the average value was used to calculate the gas permeability. Gas permeability ($P_i$, Barrer) and ideal CO₂/CH₄ selectivity ($\alpha_{CO₂/CH₄}$) were calculated using the method described in our previous work [11].

![Figure 1: Visualization of MMMs development](image)

**Table 1: Filler compositions**

| Membrane | Filler loading (wt %) |
|----------|-----------------------|
|          | CNF | GO  |
| P        | -   | -   |
| P-5G     | -   | 5   |
| P-2C/3G  | 2   | 3   |
| P-3C/2G  | 3   | 2   |
| P-5C     | 5   | -   |
3. Results and Discussion

3.1. X-Ray diffraction

Figure 2 depicts the XRD spectrum of resultant membranes at various filler composition. Initially, the pristine PPOdm membrane (Figure 2 a) exhibited a single amorphous peak at $2\theta = 14.10^\circ$ which was in good agreement with spectra reported by Khulbe et.al., [12]. Upon the addition of single filler, P-5G (Figure 2 b) and P-5C (Figure 2 e), additional low intensity peak at $2\theta = 10.24^\circ$ and $2\theta = 26.25^\circ$ which corresponded to the main reflection peak of GO and CNF were observed. The presence of these additional peaks in MMM illustrated that the filler’s crystallinity was not altered during membrane fabrication process. It also validated the dispersion of filler particles in the polymer matrix as well the polymer-filler interaction. In addition to that, the broad peak of PPOdm polymer matrix experienced a minor shift to lower angles with the addition of single filler and to higher angles with the addition of binary fillers as tabulated in Table 2.

![Figure 2: XRD spectra of a) P, b) P-5G, c) P-2C/3G, d) P-3C/2G and e)P-5C MMM](image)

From Table 2, the addition of single filler was found to increase the $d$-spacing of polymer chains and eventually produced more free volume of polymer chains into the membranes which tend to allow the gases to permeate through faster [13]. Nevertheless, upon the addition of binary fillers a slight reduction in the polymer chain distance were observed due to polymer-filler strong interaction. Sarfraz, M., & Ba-Shammakh [14] reported similar trend upon the addition of binary nanofillers (ZIF-302 and GO) into PSf polymer matrix. Moreover, the intensity of GO characteristic peak at 3C/2G filler loading was found to be very weak and insignificant as compared to 2C/3G and 5G filler loading. This indicated the exfoliation and homogenous dispersion of GO nanosheets in the PPOdm polymer matrix with the presence of CNF. Therefore, the presence of co-existing nanofillers, wherein CNF dispersed between GO nanosheets and inhibited the restacking of GO in PPOdm polymer matrix [15].

3.2. Field emission scanning electron microscope

The internal microstructure of the membranes were analysed from the FESEM morphological images, as shown in Figure 3. Pristine PPOdm membrane shows dense, non-porous and defect-free structure. From Figure 3 a) no voids or pinholes were observed. Furthermore, no phase separation was observed, in which the polymeric membrane was regularly packed. Upon the addition of fillers, the dense and non-porous structure of membrane was maintained with continuous and defect-free interconnected network morphology. However, the filler particles were observed to disrupt the polymer intermolecular chain
packing which eventually induced some wrinkles and grooves to the cross-sectional morphology of the resultant membrane. In addition to that, fracturing the MMMs in liquid N₂ caused the thin layer to fragment with slight plastic deformation due to the presence of filler particles. At 5 wt% CNF loading (Figure 3 e), the CNF particles were noticed to form small clusters due to their hydrophobic nature. At higher loading, the cohesive forces between the CNF particles dominates and eventually leads to particles agglomeration and undesirable polymer-filler interfacial defects. On the other hand, at 5 wt% of GO loading (Figure 3 b), GO nanosheets were found to disperse regularly with preferential horizontal

Table 2: d-spacing analysis of PPOₐₘ main characteristic peak at 2θ = 14.10°

| Sample | Angle (degree) | d-Spacing (Å) |
|--------|---------------|---------------|
| P      | 14.10         | 6.27          |
| P-5G   | 14.07         | 6.29          |
| P-2C/3G| 14.24         | 6.18          |
| P-3C/2G| 14.31         | 6.17          |
| P-5C   | 13.78         | 6.42          |

Figure 3: Cross-sectional morphology of a) P, b) P-5G, c) P-2C/3G, d) P-3C/2G and e) P-5C. Yellow and red boxes show the location of GO and CNF, respectively
orientation to the membrane surface. Interestingly, the filler particles were dispersed more uniformly in the polymer matrix upon the addition of binary filler. No filler agglomeration or polymer-filler interfacial defects were noticed. The sheeted morphology of GO with horizontal orientation provides significant steric effect and prevented the aggregation of CNF particles in the polymer matrix [16]. Hence, the CNF particles dispersed among GO nanosheets and loosely entangled in the polymer matrix without forming agglomerates as observed at 5C filler loading. Therefore as hypothesized earlier, the complementary interaction between these two nanofillers inhibits the formation of particle agglomeration and rendered homogenous filler dispersion properties in PPO<sub>dm</sub> polymer matrix.

3.3. Optical microscopy
Optical microscope was used to analyze the relative dispersion properties of filler particles in PPO<sub>dm</sub> polymer matrix. Figure 4 (a&amp;b) depicts the optical micrographs of P-5G and P-5C MMMs. From visual inspection, no major agglomeration was observed with the exception of several small clusters. However, the distribution was less uniform wherein some larger non-reinforced polymeric domains could be observed especially for P-5G MMM. Upon the addition of binary fillers Figure 4 (b&amp;c), the dispersion properties of fillers were relatively improved with minimum number of filler aggregates. At 2C/3G and 3C/2G loadings, the size of aggregates specifically GO nanosheets (yellow) were noticed to be reduced as compared to P-5G MMM (Figure 4 a). It might be resulted from the addition of CNF which dispersed in between the GO nanosheets and reduced the tendency of GO restacking and agglomeration in polymer matrix. Meanwhile the CNF particles dispersed more uniformly without forming any clusters or stress convergence points at the presence of GO nanosheets. Therefore, the synergistic effect of combining CNF and GO evidently improved the dispersion properties of filler particles in the polymer matrix. Furthermore, the area of filler reinforcement were enhanced with the addition of binary fillers.

![Image](image_url)

**Figure 4:** Optical micrographs of a) P-5G, b) P-5C, c) P-2C/3G and P-3C/2G MMM

3.4. Gas separation performance
At a feed pressure of 3.5 bar, the pristine PPO<sub>dm</sub> membrane exhibited high CO<sub>2</sub> permeability of 50.64 Barrer with low CO<sub>2</sub>/CH<sub>4</sub> selectivity of 7.35. Upon the addition of 5 wt% GO, the CO<sub>2</sub> permeability reduced to 45.16 Barrer while selectivity increased drastically to 40.65. GO nanosheets acted as a barrier
that impedes the direct diffusion of gases through the membranes. In addition, GO nanosheets caused the polymer chain to become more discontinuous and tortuous. At this condition, the gases diffused through the tortuous path created by GO nanosheets, which resulted in lower permeability. Simultaneously, the addition of GO enhanced the CO$_2$/CH$_4$ selectivity of pristine PPO$_{dm}$ membrane by 453%. Since, GO nanosheets increases the tortuous diffusion pathway in the polymer matrix, the polymer chain mobility was reduced while generating rigidified polymer-filler interface. The rigidified interface impedes the diffusion of larger gas molecules (CH$_4$) while favors the diffusion of small molecules (CO$_2$) with less resistance [13-14]. Moreover, the favorable interaction between the polar groups especially carboxyl (-COOH) and hydroxyl (-OH) on GO and the polar individual C-O bonds of CO$_2$ accelerates the transport of CO$_2$ through the membrane. Meanwhile, the addition of 5wt% CNF improves the CO$_2$ permeability to 129.08 Barrer with little improvement in ideal CO$_2$/CH$_4$ selectivity, 8.23. The addition of CNF disrupted the polymer chain packing and increased the polymer matrix free volume, resulting in improved gas permeability. This was confirmed by the increment in d-spacing value of polymer chain upon the addition of CNF in PPO$_{dm}$ polymer matrix in XRD analysis (Table 2). Moreover, the smooth walls of CNF allows the gases to diffuse through faster than the dense layer of polymer matrix by creating a gas pathway. Therefore it could be concluded that, P-C MMM displayed high permeability of CO$_2$ with moderate CO$_2$/CH$_4$ selectivity, while P-G MMM exhibited low CO$_2$ permeability but high selectivity for CO$_2$/C$_4$ separation. On the other hand, the addition of binary fillers enhanced the overall gas separation efficiency of MMM. At 2C/3G filler loading, the CO$_2$/CH$_4$ selectivity value reached 59.70, which was 712%, 625% and 46% higher than the selectivity reported for pristine PPO$_{dm}$ membrane, P-3C MMM and P-5C MMM, respectively. Meanwhile, the CO$_2$ permeability was measured at 62.32 Barrer which was 23% higher than pristine PPO$_{dm}$ membrane. These values were higher than the performance reported for single-filler based MMM, in which CNF acted as the pathway to increase the gas permeability, while GO nanosheets acted as selective barrier to accelerate the separation efficiency of the resultant membrane [15]. The CNF and GO dispersed regularly, disrupted the polymer chain packing and enhanced the gases diffusivity properties. Meanwhile, the hydroxyl and carboxyl group on GO had a stronger affinity with polar gas, CO$_2$ and increases the CO$_2$ solubility across the membrane. Thus, the resultant P-C/G MMM provides selective solubility of CO$_2$ polar gas and restricted CH$_4$ diffusion. CO$_2$ molecules permeated via facilitated transport mechanism combined with solution-diffusion mechanism, while CH$_4$ permeated via solution-diffusion mechanism only. Hence, the combination of 2 wt% CNF and 3 wt% GO displayed favourable synergistic effect on the gas separation performance of resultant membrane. Nevertheless, the barrier effect of GO nanosheets predominated the performance of resultant membrane, in which the superior gas permeability achieved by P-C MMM could not be obtained for P-C/G MMM.

![Figure 5: The effect of filler loading on membrane gas separation performance](image)
4. Conclusion and Recommendation

Binary fillers-based MMMs were successfully developed using two different carbonaceous nanofillers via dry phase inversion technique. The resultant membranes remained mainly amorphous with two additional filler characteristic peaks which corroborated the dispersion of CNF and GO in PPOₐm polymer matrix. The MMMs exhibited dense structure with no significant filler agglomeration and polymer-filler interfacial defects. The filler dispersion quality relatively improved for P-C/G MMMs, as compared to P-C and P-G MMMs. Moreover, significant improvement could be noticed in the gas separation performance of P-2C/3G MMM, in which the CO₂/CH₄ selectivity and CO₂ permeability were enhanced by 712% and 23%, respectively. Therefore, this technique of combining two carbonaceous nanofillers is deemed effective for efficient CO₂/CH₄ gas separation MMM fabrication.

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