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Pebax®1657/Graphene oxide composite membranes for improved water vapor separation

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Abstract

In this study composite mixed matrix membranes containing hydrophilic microphase-separated block copolymer (Pebax® 1657) and graphene oxide nanosheets were prepared using a dip coating method. Water vapor and N₂ gas permeation were measured as a function of different parameters: (i) layer thickness, (ii) content of graphene oxide (GO), and (iii) content of reduced GO. Surprisingly, a concentration of only 2 wt% of GO nanosheets well dispersed in the Pebax layer boosted the selectivity 8 times by decreasing the water vapor permeance by only 12 % whereas N₂ gas permeance decreased by 70 %. Using reduced GO instead, the water vapor permeance declined by up to 16% with no influence on the N₂ gas permeance. We correlated the permeation properties of the mixed matrix membranes with different models and found, that both the modified Nielsen model and the Cussler model give good correlation with experimental findings.

Keywords

Pebax®1657; GO nanosheets; composite membranes; dip coating; water vapor, selectivity

1. Introduction

The use of membranes to selectively remove water vapor from a humid air stream is attractive in dehydration or dehumidification processes. Membrane processes are driven by a

pressure gradient; no heat source is required and no regeneration is involved making it a greener approach with a lower environmental footprint. It is reported that energy efficiency of dehumidification processes can be enhanced up to 86% by using polymeric membranes [1].

Polymeric membranes are very attractive for gas and vapor separation because of their low cost and good selectivity. Hydrophilic polymers are good candidates for water vapor removal [2-4]. Water vapor selective membranes do not show the usual permeability/selectivity trade-off of gas separation membranes. Instead the water vapor selectivity increases generally with the permeability [5]. This means, that quite a number of polymers are available with high permeability and selectivity. Numerous studies have been carried using polymers with the hydrophilic poly (ethylene oxide) block. Metz *et al.* studied the water vapor permeation in the block copolymers of poly (ethylene oxide) PEO and poly (butylene terephthalate), where the hydrophobic PBT segment provide mechanical strength to the polymer and found that water vapor permeability strongly depends on the composition of hydrophilic part of the block copolymer [6]. Potreck *et al.* investigated the removal of water vapor from light gases using polyethylene oxide based block copolymer Pebax® 1074 and found that water vapor over nitrogen selectivity increases with an increase in water vapor activity [7]. Husken and Gaymans reported that water vapor transport through films of segmented block copolymers based on PEO and monodisperse crystallisable tetra-amide segments increased with increasing PEO concentration in the copolymer [8]. Lin *et al* studied the H₂O/CH₄ separation using composite membranes of hydrophilic microphase-separated block copolymer Pebax® 1657 and found that an increase in sweep gas flow rate increased the water vapor permeance [9]. Also in the work presented here we use a hydrophilic Pebax grade as base polymer material for the preparation of composite membranes. In the past different fillers have been applied to improve the performance of water vapor selective membranes [9-11]. In recent years graphene and graphene oxide attracted a lot of attention as

performance enhancing membrane additive. Graphene oxide is attractive as nano filler because of its high aspect ratio and its ease of functionalization with the hydrophilic polymers. GO nanosheets can be easily dispersed in water due to the presence of hydroxyl, carbonyl, epoxy, and carboxylic groups [12-15]. The high aspect ratio increases the path length molecules have to travel due to an increase in tortuosity. This increase in tortuosity affects more the diffusion of larger molecules than smaller ones. Especially water molecules can permeate fast through GO nanosheets due to hydrophilic GO pathways [16, 17].

In this work, Pebax®1657 was chosen as a hydrophilic block copolymer and graphene oxide nanosheets were used as a filler. The Pebax/GO mixed matrix films were coated on a porous PAN support by dip coating. Our assumption was that incorporation of GO nanosheets in the membranes would improve their water vapor selectivity by reducing the permeance of inert gas molecules more than the permeance of water molecules. The performance of the composite mixed membranes was investigated by determining their water vapor/N₂ gas ideal selectivity at varied amounts of GO, *reduced* GO (rGO) and the number of coating layers.

2. Experimental

2.1. Materials

Pebax® 1657 was purchased from Arkema and graphite flakes were obtained from Sigma-Aldrich. Sulphuric acid (H₂SO₄), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂) and potassium permanganate (KMnO₄) were procured from Sigma-Aldrich. Porous polyacrylonitrile (PAN) membrane was supplied by GMT GmbH, Germany. Potassium chloride, NaCl, Mg (NO₃)₂, CH₃COOK and LiCl salts were acquired from Sigma-Aldrich.

2.2. Preparation of graphene oxide and reduced graphene oxide

Graphene oxide (GO) was prepared from graphite flakes via the well-known modified Hummers method [18, 19]. Initially 2 g of graphite flakes were heated in a 100 W microwave

oven for 15 s to obtain the expanded graphite (EG) flakes as a precursor for preparation of GO. The typical procedure for GO preparation was as follows: 2 g EG flakes were placed in a 500 ml round bottom flask containing 250 ml of H_2SO_4 (98%); the resulting mixture was stirred for 90 min at 25 °C and then 10 g of KMnO_4 was added slowly under stirring condition. The dark-green colored mixture solution was stirred continuously for 24 h at 25 °C. Afterwards, the flask containing the resultant mixture was transferred into an ice bath and subsequently, 500 ml DI water was added dropwise in 3 h at 400 rpm. The temperature of the mixture solution was maintained less than 50 °C to avoid thermal explosion. The color of the mixture solution changed to golden yellow when 100 ml H_2O_2 solution (37 wt %) was added. The resulting suspension was further stirred for another 2 h. The obtained suspension was filtered and centrifuged three times with 10 % HCl at 10,000 rpm to get rid salt impurities. Then the HCl treated oxidized EG particles were centrifuged several times with DI water until the pH of the supernatant solution 5 or higher. The oxidized EG particles were exfoliated to GO during the cleaning process. Finally, a gray colored paste was obtained, which was stored in an airtight glass bottle for further use and characterizations. The reduced graphene oxide (rGO) was prepared by thermal reduction of GO at 150 °C [20]. Initially, 100 mg of GO (~ 25 g paste of GO in wet state) was dispersed in 25 ml DI water by mild sonication for 1 h at room temperature. Then, 75 ml of DMAc was added to obtain a transparent yellow-brown suspension of GO, which was transferred into a 250 ml round bottom flask. The round bottom flask along with the suspension of GO was placed into the oil bath. After that, N_2 gas was passed through the suspension for 30 min to remove the dissolved oxygen. The resulting suspension was heated at 150 °C for 5 h under inert atmosphere with continuous stirring. The color of the suspension turned black after 5 h thermal reduction reaction. The black color suspension was centrifuged several times with absolute ethanol and DI water alternatively at 10,000 rpm. A clean paste of rGO was

obtained that was dried in a vacuum oven at 60 °C for 24 h. The dried black color powder of *r*GO was stored in an air tight plastic bag for further use and characterizations.

2.3. Fabrication of composite mixed matrix membranes

The composite mixed matrix membranes were prepared from 3 wt% Pebax®1657 solution in water/ethanol mixture (30/70) by a dip coating method. The 3 wt% solution of Pebax®1657 in water/ethanol mixture was obtained by dissolving the polymer at 80 °C for 3 h. GO suspension of known concentration (1 mg/ml) in DI water was prepared by dispersing wet GO paste (4 mg/ml) in DI water using a bath sonicator for 12 h. The suspension of GO in DI water was further diluted to make suspension of various concentration in the range from 0.1 to 0.18 mg /ml. A GO suspension of known concentration was added to a 3 wt% solution of Pebax and the resulting mixture solution was stirred on a magnetic stirrer for 24 h to obtain a blend solution. After that, the blend solution was transferred into a bath sonicator and sonicated for 2 h at 50 °C for removing air bubbles. A PAN support membrane was dipped in the polymer blend solution and the coated membrane was taken out after a short time, followed by drying at room temperature for 24 h and later in a vacuum oven at 40 °C for 60 h to remove residual traces of solvents. The same procedure was applied to fabricate composite membranes with varied concentration of GO (0%, 0.2%, 0.6%, 1%, 1.6% and 2%). The fabricated composite mixed matrix membranes are denoted as M0, M1, M2, M3, M4 and M5, respectively. The loading amount of GO (wt %) in the composite mixed matrix membrane was based on the total weight of polymer in water-ethanol solvent. A similar procedure was explored to fabricate *r*GO based composite mixed matrix membrane using a 0.6 wt% dispersion of *r*GO and this membrane is denoted as M6. The free standing membranes without PAN support were fabricated from the same composition blend solutions for characterization. The loading amount of GO in the mixed matrix membranes was calculated using Eqn. (1):

$$GO \text{ loading (wt\%)} = \frac{\text{Weight of GO (g)}}{\text{Weight of GO (g)} + \text{Weight of polymer (g)}} \times 100 \quad (1)$$

2.4. Membrane Characterization

The functional groups of GO and rGO were confirmed by recording their Fourier transform infrared (FTIR) spectra on a Thermo scientific spectrometer (Nicolet iS10 model) in the range from 400 to 4000 cm^{-1} . The spectra were collected for 16 scans with a resolution of $\pm 4 \text{ cm}^{-1}$. The thickness of the mixed matrix membrane layer on the PAN support was measured via scanning electron microscopy (SEM) using a field emission scanning electron microscope (FESEM, FEI Quanta 600 series). Raman spectra of the membranes were recorded on a Raman spectrometer (Horiba LabRam Aramis) equipped with $\times 50$ objective lens (Olympus, NA 0.75) at 633 nm. To avoid any heating effect, the laser power was reduced to 0.6 mW. The wide-angle X-ray diffraction (WXR) patterns were recorded with a Bruker D8 Advance diffractometer to study the change in crystalline properties of the mixed matrix membranes. Water vapor sorption experiments for the membranes were conducted using a gravimetric sorption balance method on VTI-SA at 25 °C. The membranes were preheated at 40 °C for 6 h inside the sorption analyzer and the relative humidity was tuned by 10 % increase gradually in each step.

2.5. Gas permeation study

Single gas permeation experiments were performed using a constant volume/variable pressure test method reported earlier by our group [19]. The permeance values were calculated using Eqn. (2):

$$J = \frac{V \times 22.4}{R \times T \times A \times t} \ln \left(\frac{p_f - p_0}{p_f - p_{p(t)}} \right) \quad (2)$$

Where V is the permeate volume, R is the ideal gas constant ($\text{m}^3 \text{ bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the temperature (K), A is the membrane area (m^2) and t is time (s). p_f and p_0 , are pressures at feed side and $p_{p(t)}$ (bar) is permeate pressure.

2.6. Water vapor permeance

Water vapor permeance through the polymeric membranes was measured by standardized test methods such as ASTM E96, in which a cup is placed in an upright position (E96B) or inverted (E96BW) [21]. In the inverted cup method, the membrane is in direct contact with the liquid present in the cup. When the cup is kept in an upright position, an air layer between liquid and the surface of membrane exists. This air layer acts as an extra resistance, which affects the water vapor permeance. The water vapor transport values obtained by E96BW method are higher and therefore, the inverted cup method is often more suitable. However, the inverted cup method is not efficient in case of composite membranes since there are chances that membrane coating gets effected when it is in direct contact with water. In this work, a modified upright permeability cup method was used for water vapor transport measurements as shown in Fig. 1. A sweep gas in a continuous flow was used on the permeate side of membrane to maintain the driving force. The position of the gas inlet and outlet on the permeability cup was adjusted in such a way that water vapor from the permeate side of membrane is completely removed. A humidity and temperature transmitter (Vaisala HMT334) was used to measure the humidity and temperature on the permeate side of the membranes. Water vapor permeance through the membranes was calculated using Eqn. (3) [21]:

$$WVTR_m = \frac{dm}{dt} \times [A \times P_{sat} \times (R_1 - R_2)]^{-1} \quad (3)$$

Where A is area of the membrane, P_{sat} is the saturated vapor pressure at the test temperature, R_1 and R_2 are relative humidity at the source and the vapor sink expressed as fractions. It is reported that when the membranes are highly permeable, the water vapor permeation rate through the air gap becomes too low to maintain 100% relative humidity within the entire volume of permeability cup and driving force (Δp) is reduced [22]. Neglecting the effect of

air resistance can lead to considerable underestimation of the actual values. The apparent driving force for WVTR calculation is considered as the partial pressure difference between water vapor on the water surface and above the surface of the membrane. Whereas, the actual driving force is the partial pressure difference beneath the surface and above the surface of membrane as depicted in Fig. S1, Supporting Information. Gennadios *et al.* calculated water vapor permeance for actual driving force using Eqn. 4 by considering a correction factor for apparent and actual driving force [23]:

$$WVTR_c = WVTR_m \left[\frac{p_0 - p_2}{p_1 - p_2} \right] \quad (4)$$

Where p_1 is water vapor partial pressure beneath the surface of membrane, which can be calculated using Eqn. (5):

$$p_1 = p_T - (p_T - p_0) e^{\frac{N_w h_i}{cD}} \quad (5)$$

Where p_T and p_0 is the total atmospheric pressure and water vapor partial pressure at the surface of distilled water or salt solutions, respectively. N_w is the molar water vapor transmission rate, h_i is the air gap resistance, c is molar concentration and D is the diffusion coefficient. The correction for still air layer was also calculated Eqn. (6):

$$WVTR_c^{-1} = WVTR_m^{-1} - \frac{l}{P_a} \quad (6)$$

Where l is the air gap thickness and P_a is the vapor resistance, which can be calculated using Eqn. (7) [21]:

$$P_a = \frac{2.306 \times 10^{-5} \times P_0}{R_v \times T \times P} \left[\frac{T}{273.15} \right]^{1.81} \quad (7)$$

3. Results and discussions

3.1. Characterization of GO and reduced GO

FTIR spectra were recorded to confirm the presence of hydroxyl, epoxy and carboxylic acid groups before and after thermal reduction of GO as depicted in Fig. 2. The broad peak at 3440 cm^{-1} is assigned to O–H stretching vibrations. The intensive peaks at 1725 cm^{-1} and 1617 cm^{-1} assigned to the characteristics C=O and aromatic C=C stretching vibrations. The absorption bands at 1237 and 1095 cm^{-1} are attributed to epoxy C–O and C–O stretching vibrations [20]. Furthermore, the intensity of the peak for O–H groups is reduced and the peak for C=O groups disappear after thermal reduction of GO. These results confirm successful thermal reduction of GO at 150°C after 5 h.

3.2. Instrumental characterizations of the membranes

W-XRD patterns of the mixed membranes containing varied amount of GO are shown in Fig. S2, Supporting Information. The semi crystalline peak at $2\theta = 24^\circ$ is obtained for pristine Pebax® 1657 membrane M0 due to the crystalline region of polyamide block via inter-chain hydrogen bonding interactions [24]. The peak intensity is enhanced after incorporation of GO (Fig. S2, Supporting Information). This is attributed to increase in compactness of the membranes with varied amount of GO. The appearance of peaks in W-XRD patterns of the membranes is found to remain unchanged even at high loading of GO. These results demonstrate that semi-crystalline characteristic of Pebax polymer was not disturbed by GO nanosheets. Chen et al., obtained similar results for mixed matrix membranes based on poly(vinyl alcohol) and GO [25]. The characteristic peaks of GO have been shown earlier at $2\theta = 11^\circ$ [26]. These peaks are absent in W-XRD patterns of the mixed matrix membranes after dispersion of GO into the polymer matrix which confirms well distribution of GO and shows that GO is fully exfoliated in the Pebax matrix.

Raman spectra for pristine membrane M0 and mixed matrix membranes M1, M3 and M5 are depicted in Fig. S3, Supporting Information. It can be visualized from Fig. S3 that

two new peaks appeared at 1340 and 1610 cm^{-1} for the mixed matrix membranes. These peaks are related to the characteristic of G and D bands [11, 19]. The G band provides an information on the in-plane stretching vibration of symmetric C–C bonds of the graphitic layers (sp^2 carbon). On the other hand, D band is due to disruption of the symmetrical hexagonal graphitic lattice by internal structural defects and edged effects [27]. Further increase in amount of GO nanosheets in the mixed matrix membranes broadened the D and G peaks (Fig.S4, Supporting Information). These results validate the presence of GO nanosheets and distribution in the matrix of the fabricated membranes

The cross-sectional SEM images of the membranes are shown in Fig. 3. A dense top layer is formed on a porous PAN support membrane after coating a blend solution of Pebax and GO by dip coating. Top layers are free from any crack or defect (Fig. 3). The SEM images of the composite mixed matrix membranes are clearly showing that GO nanosheets were well distributed in the Pebax® 1657 matrix without any aggregation and void in the GO/polymer interface. The polymer adhered well to GO nanosheets due to the rubbery nature of the continuous phase (polymer) and presence of the soft segments in the polymer. Furthermore, GO nanosheets in the mixed matrix membranes are entrapped through hydrogen bonding interactions between oxygen containing functional groups (–OH and –COOH) on the GO and –NH, C=O and –OH groups of Pebax® 1657 (Fig. 4).

3.3. Water vapor sorption

The water vapor sorption at various water vapor activities and a constant temperature of 25 °C was performed to see an effect of GO loading on the water uptake capacity of the mixed matrix membranes. The obtained results are presented in Fig. 5. The sorption and desorption isotherms were similar for all membranes at varied amount of GO nanosheets and no hysteresis was found due to the rubbery nature of the polymer. Therefore, the sorption isotherms were considered and desorption isotherms are not shown in the figure. The sorption

isotherms of the membranes are linear at low water vapor activity. However, water sorption increased stronger at water vapor activities higher 0.6. A similar type of isotherms have reported by other researchers for Pebax® 1074 and Polyactive® with varying PEO and PBT contents [6, 7]. The sorption characteristics of the membranes did not get affected by GO nanosheets. It is also observed that the loading of GO nanosheets does not make any pronounce change in the water uptake property of the mixed membranes.

3.4. Pure gas permeation

Pure CO₂ and N₂ gas permeation properties of the composite membrane (M0) prepared from 3 wt% Pebax® 1657 solution were determined. The obtained values for CO₂ and N₂ gas were 36.8 and 0.63 GPU. CO₂/N₂ selectivity of the membrane M0 was 58 at 21 °C, which is close to intrinsic CO₂/N₂ selectivity of Pebax®1657 (60 at 35 °C) [28]. The obtained selectivity confirms the fabrication of defect free composite membranes from 3 wt% Pebax-1657 solution in ethanol-water mixture (7: 3) by a dip coating method. Therefore, this solution was used to fabricate mixed membranes containing GO nanosheets. The pressure normalized flux of N₂ gas with varied concentrations of GO is illustrated in Fig. 6. The permeance of N₂ gas for single layer and five layer coated mixed matrix membranes is gradually decreasing with the increase in concentration of GO nanosheets. The decline in N₂ gas permeance is more pronounced in the case of single layer coated membranes. The permeance of N₂ gas for membrane M5 containing 2 wt% GO is reduced to 70% in comparison with a pure Pebax composite membrane M0. The decline in permeance of N₂ gas leads to a higher water vapor selectivity of the mixed matrix membranes.

The permeance of N₂ gas for the composite mixed matrix membrane M6 prepared from Pebax and 0.6 wt% rGO is found very similar to the membrane with 0.6 wt% GO nanosheets. The obtained permeance of N₂ gas for thermally rGO based composite mixed matrix

membrane is in line with membranes reported by Li *et al.*; the single gas permeation through ultrathin reduced GO membranes was not altered [29].

3.5. Water vapor permeation and selectivity

The water vapor permeance values and selectivity of the composite mixed matrix membranes at varied concentration of GO are shown in Fig. 7(a,b). Membranes with one and five coatings are presented in this Figure. The water vapor permeance of the membrane M5 decreased from 6440 to 5660 GPU (*i.e.*, 12% reduction of initial value) when a single layer was coated on the PAN support membrane. The decline in water vapor permeance of the single layer coated membrane can be attributed to the concept of tortuous paths [12]. In the presence of GO nanosheets, the permeating water molecules have to follow the tortuous paths formed by the GO nanosheets. In the case of thicker membranes with 5 coating layers we see a decrease in nitrogen permeance with GO content but no reduction in water permeance could be observed with GO loading. Theoretically also for the thick membranes the water vapor permeance should decrease with GO loading. The reason for the nearly constant water vapor permeance with GO concentration lies in the experimental coating conditions. A comparison of Fig. 3a and c shows that the 5 layer coating with the graphene oxide containing Pebax (membrane M5) is thinner than the 5 layer coating with the pure Pebax. This reduction in thickness seems to counteract the reduction in water vapor permeance.

In case of the membrane M2 (0.6% loading) we compared for the single layer membrane the behavior of GO and reduced GO. The water permeance declined from 6100 to 5150 GPU. The tortuous paths formed by rGO nanosheets contain now a much lower number of hydrophilic functional groups (-OH and -COOH) (Fig. 2). Zhan *et al.*, studied the water vapor permeance properties of natural rubber and graphene based mixed matrix membranes. The water vapor permeance of the membrane was reduced to 40% after incorporation of 1.78 vol % graphene as a filler [30].

The $\text{H}_2\text{O}/\text{N}_2$ selectivity of the composite mixed matrix membranes increased with GO loading (Fig. 7b). The $\text{H}_2\text{O}/\text{N}_2$ selectivity of the membranes increased from 10,000 to 80,000 (8 times) after incorporation of 2 wt% of GO in the Pebax matrix for 5 layer coating. The high water vapor permeance can be attributed to the low friction flow of water molecules through the capillaries formed by closely spaced GO nanosheets [16], whereas the nitrogen flux is restricted. Another reason for increase in selectivity is that GO nanosheets could be tightly entrapped in the Pebax matrix through hydrogen bonding interactions with the polymer chains (Fig. 4) leading to a declined N_2 permeance [31]. The $\text{H}_2\text{O}/\text{N}_2$ selectivity of the composite mixed matrix membrane with *r*GO was low in comparison with GO based membranes for both single layer and 5-layer coatings. This is due to the reduction in water vapor permeance as a result of loss in hydrophilic groups after thermal reduction at 150 °C.

The water vapor permeance of the composite membranes was reduced with number of coating layers (Fig. S4, Supporting Information). But this decrease in permeance is not indirect proportional to the coating thickness (number of coatings). This suggests that a significant resistance to water vapor flow is arising from the support. This is in line with the results of Lin *et al.* who found that only 30% resistance is from the active Pebax layer and 70% resistance is mainly due to the composite support [9]. Tong *et al.* varied the support layer thickness and found that mass transfer of the support layer is the controlling factor to water vapor transport [32]. This is due to the fact that the sweep gas is not in direct contact with the membrane as it is on the permeate side of the composite membrane. Similar results were obtained by Nair *et al.* who found that the water permeance decreased only half when the thickness of the membrane was 10 times higher [16]. In order to support our findings, a free-standing membrane of Pebax® 1657 was made. The permeability of this membrane was measured to be 1.96×10^5 Barrer which is close to the already reported value [7]. This permeability value means that a free-standing 5.7 μm thin Pebax film should have a water

vapor permeance of 34,000 GPU. But our composite membrane with five coatings of pure Pebax and a total coating thickness of 5.7 μm (Fig. 3a) has a water vapor permeance of only 4680 GPU (Fig. 7). This shows the strong influence of the support structure (macroporous PAN plus polyester paper) on the water vapor permeation.

The water vapor permeance and $\text{H}_2\text{O}/\text{N}_2$ selectivity of the fabricated membranes are compared with other state-of-the art composite membranes (Table 1). The selectivity of the reported membranes in the literature is calculated based on the single gas experiments. It can be seen from Table 1 that the water vapor permeance and $\text{H}_2\text{O}/\text{N}_2$ selectivity of the fabricated membrane in this study are higher than that of other reported membranes in the literature.

The water vapor permeance of the composite mixed matrix membrane M2 with increase in number of coating layers of Pebax-1657 and GO nanosheets was determined at varied relative humidity. The obtained data for the membrane M2 with five coating layers is presented in Fig. 8. The relative humidity inside the permeability cup was changed using saturated solutions of various salts [40]. LiCl (11%), CH_3COOK (23%), $\text{Mg}(\text{NO}_3)_2$ (55%), NaCl (75%), KCl (85%), and DI water (100%) were used to attain the required relative humidity inside the water vapor permeability cup. It is shown that the water vapor permeance through the membrane M2 for all coating thicknesses exponentially increased with increase in relative humidity (increase in ΔP). The obtained data are consistent with the water vapor sorption capacity of the mixed matrix membranes with varied concentration of GO nanosheets (Fig. 5). This suggests that the high water vapor permeability of the membranes is based on the water solubility. At less than 55% relative humidity, a nonlinear decrease in water vapor permeance of the membrane M2 was obtained. The decrease in water vapor permeance of the composite mixed matrix membranes with reduction in relative humidity is aroused from distortion in the interlayer distance between GO nanosheets. Lerf et al. found that the interlayer distance (d spacing) between GO nanosheets in the matrix of membranes is

reduced from 11 Å to 7 Å when the relative humidity was varied from 100 to 30% [41]. Due to this reason, the freedom of movement for water molecules is restricted after reduction in d spacing and almost all capillaries in the barrier layer of the membranes became dry and nearly closed.

3.6. Prediction of the gas permeation properties

The performance of Pebax/GO composite mixed matrix membrane is shown in Fig. 9 as a plot of N₂ gas relative permeability as a function of the volume fraction of GO nanosheets. We take here as an example the Pebax layer with a GO loading of 0.6 wt.%. This translates into a volume fraction of 0.003, when we take 1.1 g/cm³ for Pebax and 2.2 g/cm³ for the GO sheets density [15]. We found a 93% decrease in thickness normalized relative permeability of N₂ gas, when we compare pure Pebax with Pebax containing GO with a volume fraction of 0.003. The decrease in relative permeability of N₂ gas at a very low GO loading proves the good barrier properties of the GO sheets for inert gases like nitrogen. The permeability of the mixed matrix membranes can be predicted by various models, which include tortuous path theory [42]. The modified Cussler and Nielsen models are the most widely used models to explain the barrier performance of mixed matrix membrane with impermeable flakes. Bharadwaj modified the Nielsen model for different filler orientations [43]. The general form of this model is given in Eqn. 8:

$$\frac{P_c}{P_m} = \frac{1-\phi}{1 + \frac{\alpha \phi}{3S} + \frac{1-\phi}{2\phi}} \quad (8)$$

Where α represents the aspect ratio of the filler; ϕ is the volume fraction; P_c is permeability of the composite; P_m is the permeability of neat polymer membrane. S explain state of the filler alignment, where $S=0$ (Eqn. 9) for randomly dispersed fillers and $S=1$ (Eqn. 10) for perfectly aligned fillers perpendicular to diffusion direction.

$$\frac{P_c}{P_m} = \frac{1-\phi}{1+\frac{\alpha}{6}\phi} \quad (9)$$

$$\frac{P_c}{P_m} = \frac{1-\phi}{1+\frac{\alpha}{2}\phi} \quad (10)$$

The Cussler model assumes that fillers are randomly dispersed inside a film. The original Cussler model modified by Lape *et al.* assumes that flake-like fillers are placed in a regular array [44]. The modified Cussler model used in this study for semi-dilute membranes having nanosheets that are well aligned is given in Eqn. 11:

$$\frac{P_c}{P_m} = \frac{1-\phi}{\left(1+\frac{1}{3}\alpha\phi\right)^2} \quad (11)$$

We also used a 3D model developed by Gusev and Lusti [45]. This model is based on the solution of Laplace equations for local chemical potential and was developed for a random array of parallel circular disks shown in Eqn. 12:

$$\frac{P_c}{P_m} = \frac{1-\phi}{e^{\left(\frac{\alpha\phi}{3.47}\right)^{0.71}}} \quad (12)$$

Fig. 9 shows the experimental data plotted with various models assuming an aspect ratio of 3000. The relative permeability of N₂ gas decreased exponentially which is in good agreement with the general shape of models proposed by Nielsen, Cussler and Gusev-Lusti. The perfectly aligned modified Nielsen model is in good agreement when the composite membranes have low GO concentrations (0-1 wt. %). This shows that in a dilute region, the contribution of GO nanosheets to reduce the composite permeability is small. However, when the concentration of GO nanosheets increases, the interstitial distance among the GO nanosheets becomes so small that they overlap and the modified Cussler model fits well to the experimental data. The relative permeability values are higher than the prediction by

Gusev-Lusti model in the dilute region and they correlate better when the GO concentration is 1.6 wt. % or more.

4. Conclusions

Composite mixed matrix membranes containing Pebax® 1657 and GO as a filler were fabricated by dip coating using a GO dispersion in an alcoholic Pebax solution and a porous PAN support. The GO nanosheets were well dispersed in the Pebax matrix without agglomeration. The addition of GO nanosheets had nearly no influence on the sorption of water vapor and led only to a slight decrease of the water vapor permeance, whereas the nitrogen permeance was reduced drastically. The incorporation of small amounts of GO nanosheets is a powerful tool to increase the water vapor selectivity of the Pebax composite membranes. An up to 8 fold increase of the water vapor/ nitrogen selectivity could be observed. The reduction of the nitrogen flux with increasing GO content could be well described with established models for the transport of gases through impermeable flake-filled membranes. There was a good agreement of experimental results with the modified Nielsen model and Lape model. The Gusev-Lusti model values were lower than the experimental data but were relatively close at higher loadings.

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Fig. 1. Schematic presentation for measuring water vapor permeation through the composite mixed matrix membranes. Humidity & temperature sensor (HMT); Mass flow meter (MFM)

Fig. 2. FTIR spectra for: (a) GO and (b) reduced GO (rGO) nanosheets.

Fig. 3. The cross-section images of the mixed matrix membranes with 5 layers: (a) M0; (b) M1 and (c) M5.

Fig. 4. Schematic presentation for hydrogen bonding interactions between Pebax® 1657 and graphene oxide nanosheets in the mixed matrix membranes.

Fig. 5. The variation in water uptake of the mixed matrix membranes with varied amount of GO nanosheets (wt%) at different water vapor activities and 25°C.

Fig. 6. Effect of GO concentration on the permeance of pure N₂ gas through the mixed matrix membranes.

Fig. 7. Effect of GO concentration and rGO on: (a) the water vapor permeance and (b) selectivity of the mixed matrix membranes with varied number of layers.

Fig. 8. The variation in water vapor permeance of the mixed matrix membranes with varied number of layer containing 0.6 wt% GO at different relative humidity (%).

Fig. 9. Comparison of the experimental data with different models for normalized permeability of N₂ gas with aspect ratio ($\alpha=3000$)

Table 1. Comparison of the water vapor permeance and selectivity of the fabricated membranes with state-of-the-art composite membranes.

Membrane material	Temperature (°C)	Water vapor permeance (GPU)	H ₂ O/N ₂ selectivity	Ref.
NaA zeolite/Ni sheet ^a	32	20042	178	10
[Emim][Tf2N] ^b	31	635	3840	33
Stabilized triethylene glycol	15-30	223	2000	34
PSU/Si-TFC ^c	30	2200	500	35
PES/PDA-TFC ^d (polydopamine)	30	3185	195	36
PEI/Pebax ® 1657 ^e	21	1800	1800	9
PSU/BA-TFC (3,5- diaminobenzoic acid)	30	2160	34	37
PSU/TFC-TiO ₂	30	1131	548	11
PVA/LiCl-SS scaffold ^f	31	1667	2800	38
PVA/TiO ₂ -SS scaffold		1524	5781	39
Pebax ® 1657/ GO (1.6% GO)	21	5000	80,000	This work

^aNa A zeolite membrane on a Ni support

^bIonic liquid membrane

^cThin film composite (TFC) membrane with silicone nanoparticles onto a PSU support

^d Polyethersulfone(PES)/polydopamine (PDA) composite membrane

^e Pebax on polyetherimide (PEI) support and ^f Polyvinyl alcohol (PVA) onto a stainless steel (SS) support.

Highlights

- Pebax/graphene oxide membranes showed extremely high selectivity for water vapor.
- The nitrogen permeability through the membranes were strongly reduced by GO addition.
- The water vapor/ N₂-selectivity increased by a factor of 8 after GO incorporation.

Accepted manuscript

Graphical Abstract