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Journal of Materials Chemistry A

ARTICLE

Polybenzimidazole-based mixed membranes with exceptional high water vapor permeability and selectivity

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Polybenzimidazole (PBI), a thermal and chemically stable polymer, is commonly used to fabricate membranes for applications like hydrogen recovery at temperatures of more than 300 °C, fuel cells working in a highly acidic environment, and nanofiltration in aggressive solvents. This report shows for the first time use of PBI dense membranes for water vapor/gas separation applications. They showed an excellent selectivity and high water vapor permeability. Incorporation of inorganic hydrophilic titanium-based nano-fillers into the PBI matrix further increased the water vapor permeability and water vapor/N₂ selectivity. The most selective mixed matrix membrane with 0.5 wt.% loading of TiO₂ nanotubes yielded a water vapor permeability of 6.8×10^{-1} Barrer and a H₂O/N₂ selectivity of 3.9×10^6 . The most permeable membrane with 1 wt.% loading of carboxylated TiO₂ nanoparticles had water vapor permeability of 7.1×10^4 Barrer and H₂O/N₂ selectivity of 3.1×10^6 . The performance of these membranes in terms of water vapor transport and selectivity is among the highest reported ones. The remarkable ability of PBI to efficiently permeate water versus other gases opens the possibility to fabricate membranes for dehumidification of streams in harsh environments. This includes the removal of water from high temperature reaction mixtures to shift the equilibrium towards products.

Introduction

The presence of water vapor in a process stream (e.g. flue gas) or enclosed space (e.g. household or office) is not always desirable and therefore, needs to be controlled. Water vapor present in flue gas can present problems like slug flow, corrosion, and erosion in the pipelines and processing equipments. A controlled level of water vapor in home or office rooms is critical for mold control and comfort. Dehumidification is an energy intensive process and it accounts for high energy consumption in buildings and space air-cooling. Effective dehumidification of fresh air can reduce up to 64% of energy consumption.¹ Membrane separation for water vapor removal from humid streams is attractive due to its ease of operation and low energy costs.

Polymeric and mixed matrix membranes have been widely studied for water vapor removal from gas streams²⁻⁶ targeting applications like flue gas dehydration, compressed air drying, dehydration of

organic compounds, natural gas dehydration, water removal from reaction mixtures to shift the equilibrium, and air dehumidification in spacecraft applications.⁷⁻¹⁰ Membranes for dehumidification can be porous and non-selective; these are used in membrane contactors¹⁻², or they can be dense and water selective. Pore-free water-selective polymeric membranes do not show the typical permeability/selectivity trade-off of gas separation membranes. Instead, the water vapor selectivity increases with the increase in water vapor permeability.¹¹ Both rubbery and glassy polymers have been used in the past for flue gas dehydration applications. Several rubbery and glassy polymers exhibit high water vapor permeabilities; however, the high glass transition temperature (T_g) and stability of glassy polymers make them attractive for challenging applications. A number of hydrophobic and hydrophilic glassy polymers, such as: polycarbonate, polyimide, poly(phenylene oxide), ethyl cellulose, cellulose acetate, sulfonated poly(amide-imide) and sulfonated poly(ether ether ketone) have been explored for fabrication of water vapor selective membranes.⁷ PBI is an aromatic heterocyclic polymer synthesized more than 50 years ago. It has a very high T_g , and excellent compression strength at elevated temperatures.¹²⁻¹³ This polymer has been used in the past for various applications like gas separations, water treatment, pervaporation, and fuel cells. It has also been proposed for blood-related dialysis and reverse osmosis membranes under high-temperature and harsh conditions.¹⁴ Phosphoric acid doped PBI has

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ARTICLE

Journal of Materials Chemistry A

been used widely for the fabrication of membranes for fuel cells, where the presence of water inside the membrane is crucial to enhance the proton conductivity.¹⁵⁻¹⁶ In addition, it has been used as a hydrophilic modifier to improve the hydrophilicity of UF membranes.¹⁷ However, it has never been thought as a promising candidate to fabricate membranes for water vapor removal applications. PBI was chosen since it is a hydrophilic polymer and can sustain high thermal and pressure conditions. This unique property of PBI makes it a good candidate to be used under stringent conditions. Moreover, it can be used in processes where removal of water vapor is important such as catalytic reactions carried out at high temperature and pressure. To demonstrate this, an esterification reaction was performed in the presence of a PBI membrane to explore the concept of equilibrium shift by the removal of water at elevated temperature.

In this work, we propose for the first time the use of PBI to fabricate polymeric and mixed matrix membranes for water vapor transport applications. Inert gas molecules permeate very slowly through PBI membrane, however the transport of water vapor molecules through its rigid densely packed matrix is very high. Molecular dynamics (MD) simulations were used to predict the changes in fractional free volume (FFV) and increase in number of hydrogen bonds as a function of relative humidity.

We further explore the effect of adding fillers with different hydrophilicity and shapes into the PBI matrix. PBI alone is a promising candidate to fabricate membranes for dehumidification and flue gas dehydration. However, an enhancement in performance of PBI is further possible by adding an appropriate filler. Nanoparticles have been dispersed into the matrix of polymers to enhance their mechanical and thermal properties. They have also been used to increase the polymer's FFV by disrupting the polymer chains, resulting in an improvement of vapor/gas separation properties of the membranes. Among the different fillers available, TiO₂ nanoparticles are particularly interesting due to their availability, stability and ease of functionalization. We hypothesized an improvement in water vapor transport properties of PBI membranes with the incorporation of TiO₂ nanoparticles, functionalized TiO₂ nanoparticles and TiO₂ nanotubes. This study presents the water vapor transport properties of PBI membranes and PBI-based mixed matrix membranes (MMM) containing different fillers. Membranes with high performance and controllable water vapor/ gas separation are presented and analyzed in detail.

Experimental details

Materials

Celazole® S26 polybenzimidazole solution was purchased from PBI Performance Products Inc., USA. The solution S26 contains 26.2 wt.% polymer and 1.5 wt.% lithium chloride dissolved in N,N-dimethylacetamide (DMAc). Titanium dioxide (TiO₂) nanoparticles (BET surface area = 35-65 m²/g), chloroacetic acid (Cl-CH₂COOH) and NaOH were purchased from Sigma-Aldrich.

Preparation of TiO₂ nanotubes

TiO₂ nanotubes were prepared by an alkaline hydrothermal treatment of TiO₂ nanoparticles in 10 M NaOH solution at 160 °C.¹⁸⁻¹⁹ TiO₂ particles (2 g) were mixed with 85 ml of 10 M NaOH solution, and the white color suspension was stirred using a magnetic stirrer at 22 °C for 24 h. The well-dispersed suspension of TiO₂ particles was then transferred into a Teflon-lined autoclave that was heated in an oven at 160 °C for 72 h. The autoclave was cooled to 22 °C after an alkaline hydrothermal treatment. The white color solid paste was taken out and immediately added into a beaker containing 250 ml of 0.1 M HCl solution. The resulting mixture was left for 24 h under stirring at 22 °C to remove an excess amount of NaOH from TiO₂ nanotubes. The white color suspension was filtered using a Whatman 41 filter paper and subsequently centrifuged several times with DI water at 5000 rpm until the pH of the supernatant solution reached to 7. The purified TiO₂ nanotubes (TNTs) were dried at 22 °C for 12 h and the traces of DI water were removed by further drying at 110 °C for 24 h. Finally, the dried TNTs were stored in a plastic zip-lock bag for characterization and use in membrane fabrication.

Preparation of carboxylated TiO₂ nanoparticles

The carboxylated TiO₂ (TiO₂-COOH; cTiO₂) nanoparticles were prepared according to a previously reported method in the literature.²⁰ The typical functionalization procedure was as follows: TiO₂ nanoparticles (1 g) were dispersed in 150 ml of DI water using a bath sonicator (VWR Co., UK) for 1 h at 40 kHz. The well-dispersed suspension of TiO₂ nanoparticles was then transferred to a 250 ml round bottom flask and thereafter, 1.5 g of chloroacetic acid was added slowly under constant stirring. The reaction was conducted at 100 °C for 7 h and the resulting suspension was cooled to RT. The white color suspension of the functionalized TiO₂ nanoparticles was then filtered using a Whatman 41 filter paper. The functionalized TiO₂ nanoparticles were washed several times with DI water until the pH of the supernatant solution turned to 7. TiO₂-COOH nanoparticles were initially dried overnight at 22 °C and then kept in a vacuum oven at 80 °C for 24 h to remove traces of the remaining DI water. The dried TiO₂-COOH nanoparticles were stored for characterizations and use in fabricating the mixed matrix membranes.

Fabrication of the mixed matrix membranes

To prepare the membrane casting solution, PBI mother solution S26 was diluted to 6 wt.% with DMAc and stirred at room temperature for 48 h. To avoid an agglomeration of the nanoparticles, the nanoparticles were initially added into a known amount of DMAc under constant stirring for 6 h and then sonicated in a bath sonicator for 2 h to achieve an adequate dispersion. PBI solution (6 wt.%) was then added into the suspension of nanoparticles in DMAc. The resulting solution mixture was stirred for 12 h followed by 4 h sonication. The polymer concentration in the solvent was 2 wt.% and the loading of TiO₂ nanoparticles varied from 0.5 to 20 wt.%. The well-dispersed blend solution was ring cast on a silicon wafer and dried in vacuum oven at 80 °C for 48 h, and further at 200 °C for 24 h to remove traces of DMAc solvent. A similar

procedure was adopted to fabricate the mixed matrix membranes using TiO₂ nanotubes and 6 wt.% PBI solution. The loading amount of TiO₂ nanoparticles or TNTs (w.t. %) in the mixed matrix membranes was based on the total weight of PBI polymer in the solvent and it was calculated according to Equation (1).

$$\text{TiO}_2 \text{ loading (wt\%)} = \frac{\text{Weight of TiO}_2 (\text{g})}{(\text{Weight of TiO}_2 (\text{g}) + \text{Weight of polymer (g)})} \times 100 \quad (1)$$

Membrane characterization

The surface chemistry of the modified nanoparticles, TiO₂ nanotubes and characteristic functional groups of the membranes was identified by 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 ± 4 cm⁻¹. To evaluate an effect of relative humidity on the FTIR spectra of pristine PBI membrane, the membrane samples were placed inside the air tight vessels in which relative humidity was controlled using saturated salt solutions. For these measurements, the membrane samples were equilibrated inside the salt solutions for two weeks.

SEM images and EDX analysis were obtained using FEI Quanta 200. The SEM images were recorded at an acceleration voltage of 5 kV and at 20 kV for EDX analysis. Cross-section of the samples were prepared by fracturing the membranes after exposing them in liquid nitrogen for 2 min. The membrane samples were coated with a thin film of Iridium to reduce charging during imaging.

Transmission electron microscopy (TEM) was used to see the distribution of TiO₂ nanoparticles or nanotubes inside the membranes and their corresponding size. TEM images were obtained using a FEI Titan 80–300 CT operated at 300 kV. To prepare cross-section membrane samples for TEM analysis, the membranes were embedded in a low-viscosity epoxy resin (Agar R1165) and sectioned with a Leica EM UC6 ultramicrotome.

The wide-angle X-ray diffraction (WAXRD) patterns were recorded on Bruker D8 Advance diffractometer to study the changes in crystalline properties of TiO₂ nanoparticles, nanotubes and the mixed matrix membranes.

Thermal decomposition of the membranes was examined by conducting thermogravimetric analysis (TGA) using TA Instruments (Q5000IR) under air flow. The samples were equilibrated at 100 °C under air and the temperature was raised to 800 °C at a rate of 3 °C/min. Finally, the temperature was maintained constant for 20 min.

Water vapor sorption experiments for the membranes were conducted at 25 °C using a gravimetric sorption balance method on a VTI-SA sorption analyzer from TA instruments, USA. Once the mass uptake reached equilibrium for a given activity, the system proceeded to the next programmed step for activity. Equilibrium was considered when the mass uptake reached below a threshold limit (0.001% mass change in 120 min) over a specified time interval. The sample was dried inside the sorption analyzer chamber at 100 °C for 2h prior to the measurements to achieve a constant

weight. Sorption measurements were recorded for water activities in the range of 0 to 0.95 with gradual increment of 0.1. Desorption measurements were also recorded over the entire range of activity. The equilibrium sorption concentration of water vapor inside the membrane was calculated from equilibrium mass uptake of the membrane sample as given in Equation (2).

$$C = \frac{(M_\infty - M_i)V_{H_2O}}{V_p M_{w,H_2O}} \quad (2)$$

where C is the equilibrium concentration of the penetrant (cm³STP/cm³Poly), M_∞ and M_i are the final and initial mass of the polymer, respectively, M_w is the molecular weight of water, V_p is the volume of polymer (cm³) and V_{H_2O} is the volume of one mole of water at standard temperature and pressure (22414 cm³).

Performance of the mixed matrix membranes

Gas permeation study: Pure gas permeance was obtained using a constant volume/variable pressure test method. Single gas permeance through the membranes was calculated according to the Equation (3).

$$J = \frac{V \times 22.4}{R \times T \times A \times t} \ln \left(\frac{p_f - p_0}{p_f - p_{p(t)}} \right) \quad (3)$$

where V is the permeate volume (m³), R is the ideal gas constant (m³ bar. mol⁻¹. K⁻¹), T is the temperature (K), A is the membrane area (m²) and t is time (s), p_f is the feed pressure, p_0 is the permeate pressure at time zero and $p_{p(t)}$ is the pressure at the end of the measurement.

Performance of the membranes for water vapor transport: The water vapor permeance was acquired using a modified permeability cup test method reported earlier by our group.²¹ The schematic presentation for water vapor permeance measurement is shown in Figure S1 (ESI). The relative humidity on the permeate side of membrane was modulated using a sweep gas in a continuous flow to maintain the driving force. 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 Equation (4).²²

$$WVTR_m = \frac{dm}{dt} \times \left[A \times P_{sat} \times (R_1 - R_2) \right]^{-1} \quad (4)$$

where A is the membrane area, P_{sat} is the saturated vapor pressure at the test temperature, R_1 and R_2 are the relative humidity at the source and the vapor sink. It is reported that for highly permeable membranes the water vapor permeation rate through the air gap becomes too low to maintain 100% relative humidity within the entire volume of permeability cup resulting in a declined driving force.²³ Neglecting the effect of air resistance can lead to considerable underestimation of the actual values. The apparent driving force for WVTR calculation is often considered as the partial pressure difference between the water vapor at the water surface and above the surface of membrane. Whereas the actual driving force is the partial pressure difference beneath the surface and

ARTICLE

Journal of Materials Chemistry A

above the surface of membrane (Figure S2, ESI). The water vapor permeance for the actual driving force is calculated using Equation (5) by considering a correction factor for apparent and actual driving force.²⁴

$$WVTR_c = WVTR_m \left[\frac{p_0 - p_2}{p_1 - p_2} \right] \quad (5)$$

where p_1 is the water vapor partial pressure beneath the membrane surface, which can be calculated according to the Equation (6).

$$p_1 = p_T - (p_T - p_0) e^{\frac{N_w h_i}{cD}} \quad (6)$$

where p_T and p_0 are the total atmospheric pressure and water vapor partial pressure at the surface of distilled water or salt solutions. 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.

Computational details

MD simulations of PBI-water mixture were carried out using Material Studio version 8.0 and the COMPASS force field was used to assign charge and force field parameters for the simulations. The amorphous cells of the PBI-water system were constructed using an amorphous module by mixing two PBI chains (each chain has 10 repeat units) with various numbers of water molecules based on the relative humidity from the experiment. From the energy minimized amorphous cell, MD simulations at 298 K were carried out using the Forcite module; isothermal-isobaric (NPT) and isothermal-isopycnic (NVT) ensembles were used for the equilibration (100 ps) and production run (1000 ps), respectively. The time step of the simulation was set to 1 fs. The Andersen and Berendsen methods were used for temperature and pressure control. Long range Coulombic interactions were taken into account with the Ewald sum method, and the non-bonded energy was calculated with a cut-off distance of 9.5 Å. A probe radius of 1.32 Å was used to calculate the fractional free volume using the Equation (7).

$$FFV = \frac{V_f}{V_o + V_f} \quad (7)$$

where V_f and V_o , respectively, are the free volume and occupied volume of the polymer matrix in a cell.

RESULTS AND DISCUSSIONS

Characterization of TiO₂ nanoparticles and TiO₂ nanotubes

FTIR spectra of TiO₂ nanoparticles and TiO₂ nanotubes are shown in Figure 1a. In the FTIR spectrum of cTiO₂ nanoparticles the characteristic peak at 1681 cm⁻¹ is attributed to the stretching vibrations of carbonyl (C=O) group. The absorption band at 2980 cm⁻¹ is ascribed to the methylene (-CH₂) stretching vibrations. These results confirm carboxylation of TiO₂ nanoparticles. Furthermore, the broad absorption bands at 3334 cm⁻¹ are the characteristic peaks for hydroxyl groups that exist in TiO₂ nanoparticles, alkali treated TiO₂ nanoparticles and TiO₂ nanotubes. FTIR spectra of TiO₂ nanotubes show a broad peak for hydroxyl group in the range of 3000-3400 cm⁻¹, which is due to the preparation procedure where a strong hydrothermal treatment was performed in a strong base solution.

FTIR spectra of PBI and the mixed matrix membranes are shown in Figure 1b. All the characteristic peaks of PBI appear in the spectrum. The peak at 690 cm⁻¹ is assigned to the C-H bending vibration of 3, 4-disubstituted biphenyl moiety. The absorption band at 798 cm⁻¹ is associated with heterocyclic ring vibration, 1440 cm⁻¹ to the C-H stretching vibration of three adjacent hydrogen atoms present in the substituted benzene rings. The peak at 1603 cm⁻¹ is ascribed to C=C stretching and ring vibration characteristics of conjugation between benzene and imidazole rings. The narrow peak at 1725 cm⁻¹ in the FTIR spectra of PBI membrane is attributed to the localized normal vibrations of phenyl moieties available in PBI.²⁵ The broad intense peaks are observed in the range of 3000-3400 cm⁻¹ and these peaks appeared due to N-H stretching vibrations. It is also noticed that the peaks in the range of 3000-3400 cm⁻¹ became broad and their intensities reduced after addition of TiO₂ nanoparticles and TiO₂ nanotubes in the matrix of PBI membranes (Figure 1b). This observation validates hydrogen bonding interactions between N-H groups of PBI and -OH groups present in TiO₂ nanoparticles or in TiO₂ nanotubes.²⁶

ATR-FTIR spectra of pristine PBI membranes were also recorded at different relative humidity. As shown in Figure 1c, the area of the broad absorption band (3000-3400 cm⁻¹) due to adsorption of water evolved progressively with the increase in relative humidity. However, other peaks do not change and there is no pronounced effect observed with the change in relative humidity below 3000 cm⁻¹. The peaks at 3150 and 3370 cm⁻¹ are associated with stretching vibration of hydrogen bonded N-H and free N-H groups.²⁷ This observation is clearly indicating an improvement in water binding ability of pristine PBI membrane with increasing relative humidity

Journal of Materials Chemistry A

ARTICLE

Figure 1: ATR-FTIR spectra for: a) TiO₂ nanoparticles, cTiO₂ nanoparticles and TiO₂ nanotubes; b) PBI and the mixed matrix membranes and c) PBI membranes at varied relative humidity (%).

Instrumental characterizations of the membranes: The WXR analysis of the mixed matrix membranes was carried out to evaluate the crystallinity change in TiO₂ nanoparticles or nanotubes and after incorporation into the PBI matrix. Figure S3a (ESI) shows similar WXR patterns of the modified and unmodified nanoparticles, indicating that surface functionalization (i.e. carboxylation reaction) did not change the crystalline structure of TiO₂ nanoparticles. The crystalline phase of the TiO₂ nanotubes and nanotube-containing membranes (Figure S3b, ESI) did not change as well and overall crystallinity was maintained. The crystal planes can also be observed in the TEM images of TiO₂ nanotubes.

It can be seen from Figure S3b (ESI) that PBI membranes show a peak at $2\theta = 21.5^\circ$ which is associated with the convolution of an amorphous and a crystalline region. The WXR patterns of the mixed matrix membranes exhibited the characteristic peak for TiO₂ at $2\theta = 25.3^\circ$. This indicates that the crystallinity of TiO₂ fillers remains unchanged after incorporating into the matrix of PBI

membrane and these fillers are still in anatase phase.²⁸ The intense peaks in the mixed matrix membranes appeared due to high loading of TiO₂ nanoparticles (10 wt.% for the analyzed samples).

TEM analysis was performed to determine the change in morphology before and after carboxylation of TiO₂ nanoparticles as well as TiO₂ nanotubes as shown in Figure S4a-d (ESI). The morphology of TiO₂ nanoparticles did not alter after carboxylation at 100 °C. TEM images of TiO₂ nanotubes are revealing that the nanotubes are open-ended with an approximately 30 nm diameter which is in agreement with previously reported values.²⁹ TEM images of PBI mixed matrix membranes containing TiO₂ nanoparticles and TiO₂ nanotubes at low-magnification show the presence of nanoparticles and nanotubes in the PBI matrix. It is clear from the low magnification images that some nanoparticles and nanotubes form aggregate in the PBI matrix (Figure 2a and Figure 2c). Moreover, high-magnification TEM images show that the agglomeration of nanoparticles and nanotubes is not very high as shown in Figure 2b and Figure 2d. Moreover, these images also depict the uniform distribution of fillers throughout the entire PBI matrix.

Journal of Materials Chemistry A

ARTICLE

Figure 2: TEM images of PBI-based mixed matrix membranes at low and high magnification containing 10 wt.% TiO_2 nanoparticles (a and b) and 10 wt.% TiO_2 nanotubes (c and d).

Additional information on the morphology of the fabricated membranes as well as the distribution of different types of TiO_2 fillers is acquired with the help of SEM-EDX. It is observed that the incorporated fillers have good compatibility with the matrix of PBI as shown in Figure 3.

EDX line analysis for titanium (Ti) element in the cross-section of the membranes indicates a homogeneous distribution of the fillers throughout the entire cross-section of mixed matrix membrane (Figure 4).

TGA analysis data for pristine PBI and the mixed matrix membranes at varied loadings of TiO_2 nanoparticles is shown in Figure S5 (ESI). PBI shows a visible weight loss below 200 °C due to the absorbed water, therefore TGA thermograms were calibrated using the weight loss at 200 °C.³⁰⁻³¹ The weight loss of all the membranes is also shown in the inset table of Figure S5 (ESI). Liu *et al.* used TGA coupled with mass spectroscopy and reported that reduction in weight below 300 °C was predominantly due to desorption of water. This reduction in weight is reversible which is a combination of the absorbed water and reversible hydrolysis of the

benzimidazole moieties.³² We found 10.5% weight loss till 450 °C for pristine PBI, which may be due to the presence of impurities in the commercial PBI solution.³³ It is also proposed that the degradation of PBI begins with the hydrolysis of imidazole moieties, which ends with the production of amine amide structures.³⁴ It is

clear from the Figure S5 (ESI) that the thermal stability of the mixed matrix membranes has improved after addition of the varied amount of TiO₂ nanoparticles. Similar trends are visualized for mixed matrix membranes containing TiO₂-COOH nanoparticles or TiO₂ nanotubes as presented in Figure S6 and Figure S7 (ESI).

Figure 3: Cross-section images for PBI-based mixed membranes containing 10 wt.% of TiO₂ nanoparticles (a) and (b) TiO₂ Nanotubes. Inset figures show high magnification images of TiO₂ nanoparticles and TiO₂ nanotubes in PBI matrix.

Figure 4: EDX line scans for Ti on the cross-section of PBI membranes containing TiO₂ fillers. The secondary electron images show the area used for analysis; x-axis of the graphs indicates the line followed during EDX analysis. a) 1% TiO₂ NP; b) 10% TiO₂ NP; c) 10% cTiO₂ NP and d) 10% TiO₂ NT.

Water vapor sorption

The water vapor sorption and desorption isotherms of pristine PBI membrane at various vapor activities were recorded at 25 °C as depicted in Figure 5a. The water vapor sorption was performed only for pristine PBI membranes to see the effect of water vapor upon fractional free volume and to calculate hydrogen bonding interactions.

Water vapor sorption, especially for hydrophilic polymeric membranes is a complex process since it involves continuous change in structure and properties due to swelling or plasticization.

The gravimetric sorption analysis data confirm the adsorption of water by PBI membrane. It can achieve a water uptake as high as 35% at 25 °C when the activity is 0.95 ($a=p/p_0$). This uptake is higher than previously reported values in the range from 15 to 25%.^{14,25,35-37} To validate the high water uptake capacity of PBI membranes, sorption analysis was done several times under rigorous equilibrium conditions. The average of 5 measurements data is presented in Figure 5a along with the corresponding error bars.

The water vapor sorption in glassy polymers is often characterized by the dual-mode sorption isotherms at low water vapor activities. According to this model, the initial gas sorption occurs in the excess free volume portion of the polymer matrix and upon hole

ARTICLE

Journal of Materials Chemistry A

saturation, gas molecules dissolve in the equilibrium dense portion of the polymer matrix. This model is described by Equation (8).³⁸

$$C = C_H + C_L = K_D p + \frac{C'_H b p}{1 + b p} \quad (8)$$

where C is the concentration of water vapor in the material ($\text{cm}^3\text{STP}/\text{cm}^3\text{Poly}$), p is the pressure (atm), K_D is the solubility coefficient in Henry's law region ($\text{cm}^3\text{STP}/\text{cm}^3\text{Poly.atm}$), C'_H is the Langmuir saturation capacity parameter ($\text{cm}^3\text{STP}/\text{cm}^3\text{Poly}$), and b is the Langmuir affinity parameter (atm^{-1}) that characterizes the affinity between the penetrant and the Langmuir sites. A dual-mode model fit using Equation (8) is plotted in Figure 5b up to 0.6 activity

(solid line) for the pristine PBI membrane, and the corresponding model parameters are tabulated in Table S1 (ESI). The experimental results are in excellent agreement with the model data at low water vapor activities. This shows the clusters of water molecules are not formed in pristine PBI membrane at low water vapor activities, otherwise the water vapor sorption isotherms would deviate from dual-mode sorption model.³⁹ However, there was a significant upturn when the relative pressure was higher than 0.6. The large degree of upturn at high partial pressure region could be due to swelling or clustering of water molecules in the PBI membranes.⁴⁰

Figure 5: (a) Water vapor sorption (closed squares) and desorption isotherm (open squares) for PBI membrane under different water vapor activity ($a=p/p_0$) at 25 °C, (b) Dual-mode sorption model for PBI sorption (c) Flory-Huggins sorption model for PBI membranes, (d) phenomenological explanation of cluster formation.

Water vapor sorption in glassy polymers at high water vapor activities showing an upturn in the solubility can be modeled using different models. A modification in the dual-mode model has been proposed by Feng recently.⁴¹ Other research groups have also proposed different modifications to the classical dual-mode model.⁴²⁻⁴³ Flory-Huggins theory was originally developed for rubbery polymers. The experimental data for pristine PBI membranes, presented in Figure 5a, can be adequately described in the entire range of partial pressures with the Flory-Huggins

approach. The Flory-Huggins equation is presented in Equation (9).⁴⁴

$$\ln\left(\frac{p}{p_0}\right) = \ln\phi + (1-\phi) + \chi(1-\phi)^2 \quad (9)$$

where p and p_0 are the penetrant pressure and saturation vapor pressure at the studied temperature, χ is the polymer-penetrant interaction parameter, ϕ is the volume fraction of penetrant absorbed by the polymer and can be calculated using Equation (10).⁴⁵

$$\phi = \frac{C \times \left(\frac{V}{22414} \right)}{1 + C \times \left(\frac{V}{22414} \right)} \quad (10)$$

where C is the concentration ($\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ Poly}$) and V is the molar volume of water at 25°C

The Flory-Huggins interaction parameter (χ) can be calculated with the help of an empirical power series expression suggested by Gundert and Wolf given in Equation (11).⁴⁶ The best fit of these parameters give rise to the interaction parameter.

$$\chi = \chi_0 + \chi_1(1-\phi) + \chi_2(1-\phi)^2 \quad (11)$$

Water vapor sorption over the entire activity range (0-0.95) is plotted with the Flory-Huggins model and is shown in Figure 5c. The amount of water absorbed in the polymer follows an exponential increase as predicted by the Flory-Huggins theory coupled with the interaction parameter.

Desorption isotherm shows a big hysteresis and the water desorption does not reach to 0 wt.% when the activity is zero (Figure 5a). The slight increase in the desorption peak with decreasing humidity implies that the imbibition of water vapor in the PBI membrane occurs at high humidity. Most of the adsorbed water could be desorbed from PBI membrane with reduction in water vapor activity, but complete desorption of water molecules is inhibited by the strong hydrogen bonding interactions between adsorbed water molecules and N-H groups existing in PBI as discussed in the previous section. Although the equilibrium conditions used are very strict (i.e., 0.001% change for 120 min), it is possible that they are not sufficient for complete desorption of water molecules. Berens and Wessling *et al.*, interpreted this hysteresis as the induction of new free volume sites and subsequent filling of an extra free volume during the sorption cycle.⁴⁷⁻⁴⁹ Rivin *et al.* explained the sorption hysteresis using the slow volume relaxation of the hydrophilic clusters in response to the change in water vapor activity, which results as high membrane swelling at a known water vapor activity.⁵⁰ It is also reported that a high amount of free volume is available during desorption, and significant plasticization at very low activities results in high water vapor concentration during desorption runs.⁴⁹

The third part of the sorption isotherm (convex to the water vapor activity axis) at high activities deviates from the dual-mode and conforms to an exponential increase in water uptake indicating swelling or clustering of water molecules in the polymer matrix (also known as self-hydrogen bonding of water molecules). The water molecules associate with neighboring molecules to increase

the diameter of penetrant. There are chances of either swelling or cluster formation in case of our PBI membranes. We did not measure the diffusivity of the membranes but if an increase in solubility is accompanied by an enhancement in diffusion coefficient, it shows swelling of the membrane, providing an evidence of segmental mobility. On the other hand, the chances of cluster formation of water molecules are high when the diffusion coefficient decreases with increase in solubility.⁴⁵

The inception of water clusters formation can be explained with the help of a mathematical expression proposed by Zimm and Lundberg with the so called cluster integral (G_{11}) expressed in Equation (12).⁵¹

$$\frac{G_{11}}{V_1} = -\left(1-\phi\right)\left(\frac{\partial(a/\phi)}{\partial a}\right)_{p,T} - 1 \quad (12)$$

where G_{11} is the cluster integral, a is the water vapor activity (p/p_0) and ϕ is the volume fraction of the penetrant. The cluster factor $\phi(G_{11}/V_1)$ is the average number of molecules in excess of the average penetrant concentration in the neighborhood of a given penetrant molecule. The value $\phi(G_{11}/V_1) > 0$ is an indication of cluster formation. Figure 5d shows application of Equation (12) to the sorption data for high water vapor activities. It is evident from Figure 5d that cluster formation or swelling starts when the activity is more than 0.7. The change in diffusion coefficient with variation in water vapor activity can be helpful in establishing a difference between swelling and cluster formation. However, the physical interpretation of Figure 5d is not a definite proof of cluster formation because there are notable differences observed when this technique or some other techniques like FTIR spectroscopy is explored.⁵² Shi *et al* found that the increase in pervaporation dehydration of alcohols was mainly due to the increase in diffusivity selectivity when they used ZIF-8 filler in the PBI matrix.⁵³

MD simulations for PBI-water interactions: Figure 6 (a-d) shows the snapshot of PBI-water mixtures at an activity of 0, 0.6, 0.8 and 0.95.

It shows clearly that the packing of polymer chains in the amorphous cell is different with various water vapor concentrations. We hypothesized that the intermolecular bonding interactions between PBI chains and water molecules increase with increasing humidity. This hypothesis was supported by MD simulation analysis where hydrogen bonding interactions increased with increasing humidity (Figure 6f).

Figure 6: Snapshots of MD simulations (a-d) showing the changes in FFV probed by H_2O when water vapor activity increases (a) $a = 0$, (b) $a = 0.6$, (c) $a = 0.8$, (d) $a = 0.95$, (e) Change of FFV with increase in water vapor activity, (f) Increase in number of hydrogen bonds with the increase in water vapor activity.

As anticipated, the free volume of the polymer matrix decreased owing to the increase in hydrogen bonding interactions as shown in Figure S8 - S11 (ESI). To further explain this phenomenon, we calculated FFV of the polymer with and without water molecules. Furthermore, the total number of hydrogen bonds in the system were calculated and the results confirmed the decrease in FFV of the polymer with increase in water activity (Figure 6f). This can be attributed to increase in hydrogen bonding interactions. The calculated FFV and the number of hydrogen bonds are in good agreement with experimental observations. Other researchers also concluded that PBI shows strong affinity to water due to the sorption characteristics in water.⁵⁴

Water vapor permeation and selectivity

Effect of TiO_2 nanoparticles loading: The water vapor permeability and the water vapor/ N_2 selectivity of the pristine PBI and the mixed matrix membrane are shown in Figure 7a. The water vapor permeability of the PBI membrane is higher than 40,000 Barrer with very high water vapor/ N_2 selectivity in the order of 10^6 . The high permeability is a result of the water affinity of the PBI polymer. According to the gravimetric sorption analysis data (Figure 5a), PBI can absorb 35 wt.% water at RT. This makes PBI a good candidate for water vapor permeation among other hydrophilic glassy polymers like sulfonated poly (ether ether ketone), ethyl cellulose, cellulose acetate and sulfonated poly (ether sulfone). Brooks et al. conducted ^1H NMR analysis for adsorption of water in PBI and reported that most of the water molecules in PBI are effectively

mobile. They suggested two possible ways for occurrence of hydrogen bonding interactions between water and amine. The first possibility is that two water molecules are attached with the imidazole ring with one water molecule acting as a proton acceptor and the other as a proton donor. In this way four water molecules are attached to each repeat unit of PBI. While in the second possible way, one water molecule is attached to two neighboring imidazole rings from the adjacent polymer chains.³⁷

The water vapor permeability of phosphoric acid doped PBI reported in the literature is 3882 Barrer and 71674 Barrer (measured at 160°C).⁵⁵⁻⁵⁶ The water vapor transport reported for phosphoric acid doped PBI is high because the measurements were conducted at a very high temperature. Gibson showed that water vapor transport increases exponentially with increasing temperature. He tested 9 different polymers and found the same pattern for all the studied polymers. The change in water vapor diffusion resistance was small when the temperature raised gradually from 3°C to 40°C . The increase in water vapor transport with temperature was mainly due to the fundamental relationship between temperature and saturation vapor pressure of water.⁵⁷ The measured water vapor/ N_2 selectivity for pristine PBI membrane was also very high as compared to the traditional polymers mentioned above. The reason for high selectivity is the high density chain packing of PBI resulting in low gas permeabilities for inert gases.³⁰ This translates ultimately in high selectivity against water vapor which is capable to travel fast through the matrix of PBI.

Figure 7: The water vapor permeability and water vapor/N₂ selectivity of the mixed matrix membranes at varied amount of (a) TiO₂ nanoparticles (0.5%, 1%, 10% and 20%), (b) cTiO₂ nanoparticles (0.5%, 1% and 10%), (c) TiO₂ nanotubes (0.5%, 1%, 10% and 20%), (d) 1% loading of TiO₂ nanoparticles, cTiO₂ nanoparticles and 0.5% loading of TiO₂ nanotubes.

PBI can sustain high temperatures, it can be used to improve the percent yield of an esterification reaction at elevated temperature. Esterification is an equilibrium limited reaction. Using a PBI membrane (which allowed selective removal of water vapor) instead of a closed reactor (Figure S12, ESI) improved the ester yield up to 18% (Figure S13, ESI). Four different kind of esters were tested and ester formation was confirmed by ¹HNMR (Figure S14–Figure S18, ESI).

The water vapor permeability of the mixed matrix membrane enhanced gradually with the increase in loading of TiO₂ nanoparticles. Both water vapor permeability and selectivity improved with the loading of TiO₂ nanoparticles (Figure 7a). The water vapor permeability of the mixed matrix membrane has increased because the hydrophilicity of the membrane is improved after incorporating TiO₂ nanoparticles.^{58–59} It is clear from FTIR spectra (Figure 1a and 1b) that the peaks in the range from 3000–3400 cm⁻¹ (due to the stretching vibration of –OH and N–H groups)

broaden when TiO₂ nanoparticles are incorporated into the mixed matrix membranes. The water vapor permeability remains same and water vapor/N₂ selectivity decreases when more than 1 wt% of TiO₂ nanoparticles are incorporated. This is due to the substantial change in free volume through disruption in the polymer chain packing after the introduction of TiO₂ nanoparticles leading to an increase in gas permeability of the mixed matrix membranes.^{60–63} The increase in gas permeability is responsible for decline in the water vapor/N₂ selectivity. The mixed matrix membrane containing 1 wt.% TiO₂ nanoparticles has the best combination of water vapor permeability and high water vapor/N₂ selectivity.

Effect of carboxylated TiO₂ nanoparticles loading: The effect of carboxylated TiO₂ nanoparticles on membrane performance is presented in Figure 7b. The water vapor permeability of the mixed matrix membranes containing cTiO₂ nanoparticles increase to 75% in comparison with the pristine PBI membrane. The water vapor permeability of the mixed matrix membranes is highly dependent on the loading amount of cTiO₂ nanoparticles. The improvement in

ARTICLE

Journal of Materials Chemistry A

water vapor permeability and selectivity of the mixed matrix membranes can be correlated with hydrophilicity and creation of additional path for water transport.⁶⁴ It is well-known that cTiO₂ nanoparticles are highly hydrophilic and this leads to an overall improvement in hydrophilicity of the mixed matrix membranes after incorporating a high content of cTiO₂ nanoparticles. In addition, the introduction of carboxylic acid (-COOH) groups in the matrix of membranes has a positive impact on hydrophilicity as validated from water absorption measurements.⁶⁵⁻⁶⁶ The cTiO₂ nanoparticles have hydroxyl (-OH) and carboxylic acid (-COOH) groups, which are introduced in the mixed matrix membranes after addition of cTiO₂ nanoparticles. Another factor is the creation of excess paths for water vapor permeation when cTiO₂ nanoparticles are added. The addition of cTiO₂ nanoparticles above a certain threshold increases N₂ gas permeability, decreasing the water vapor/N₂ selectivity. The mixed matrix membrane containing 1 wt.% of cTiO₂ nanoparticles has the highest water vapor permeability and water vapor/N₂ selectivity under the optimized experimental conditions.

Effect of TiO₂ nanotubes loading: Figure 7c shows variation in water vapor permeability and the water vapor/N₂ selectivity of the mixed matrix membranes at varied concentration of TiO₂ nanotubes. The water vapor permeation properties of the mixed matrix membranes increase after addition of TiO₂ nanotubes into the polymer matrix. It can be visualized from Figure 1a that TiO₂ nanotubes have high number of hydroxyl groups which are produced on the inner and outer wall of the TiO₂ nanotubes after an alkaline treatment of TiO₂ nanoparticles at high temperature.⁶⁷ The high concentration of -OH groups in the TiO₂ nanotubes is responsible for an increase in hydrophilicity and water vapor permeability. The water vapor/N₂ selectivity of the mixed matrix membranes increased with the addition of TiO₂ nanotubes up to 0.5%. However, N₂ gas permeability increased when the loading of the TiO₂ nanotubes exceeded 0.5%, resulting a decline in selectivity. The decrease in N₂ gas permeability at low amount of TiO₂ nanotubes can be attributed to the increase in the tortuous path. There are chances of agglomeration of TiO₂ nanotubes when the loading is more than 0.5 wt.%. This can create nonselective voids, which decrease the water vapor/N₂ selectivity.

Figure 7d and Table S2 summarizes the performance of the best membranes among the tested membranes in this work. A remarkable improvement is noticed in performance properties of the mixed matrix membranes fabricated from PBI with different morphology and functionality of TiO₂-based fillers. The highest water vapor/N₂ selectivity of the mixed matrix membrane is attained at 0.5% loading of TiO₂ nanotubes, whereas the incorporation of 1% cTiO₂ nanoparticles provides the highest water vapor permeability and high water vapor/N₂ selectivity.

The water vapor permeability and water vapor/N₂ selectivity of the fabricated membranes are compared with other reported membranes in the literature as shown in Figure 8. The mixed matrix membranes manufactured from PBI and TiO₂-based fillers have high water vapor permeability and selectivity in comparison with other reported data in the literature.

Figure 8: Comparison of water vapor permeability and selectivity of the fabricated membranes with state-of-the-art membranes.

Conclusions

We have demonstrated that PBI is a promising material for the fabrication of membranes with high water vapor permeability and H₂O/N₂ selectivity. Water vapor sorption data could be well explained with the dual-mode sorption model at low partial pressures; over the entire range of water activity the Flory-Huggins approach gave the best fit. Moreover, MD simulations showed a decrease in FFV with an increase in relative humidity, which was in good agreement with experimental observations.

PBI is relatively inexpensive commercially available polymer, it has high chemical and thermal stability, and its permeability for inert gases is very low. PBI-based mixed matrix membranes fabricated using different TiO₂-based fillers showed more promising performance for water vapor transport. TiO₂ nanoparticles, cTiO₂ nanoparticles and TiO₂ nanotubes were highly compatible with PBI in the fabrication of the mixed matrix membranes as validated by TEM analysis. Even a small amount of the filler incorporated in the PBI matrix was sufficient for large improvement in water vapor permeability and H₂O/N₂ selectivity of the mixed matrix membranes. The water vapor permeability and water vapor/N₂ selectivity of the mixed matrix membranes in comparison to pristine PBI membrane almost doubled after incorporating a small amount of TiO₂ nanotubes (0.5 wt.%). The developed mixed matrix membranes have the potential of industrial applications for flue gas dehydration and energy-efficient dehumidification, particularly in harsh environments. For example, an integrated vapor permeation/esterification system with PBI membrane showed an increase in ester yield due to an efficient and selective removal of water molecules. There are promising applications, yet to be explored for PBI membrane in industrially relevant equilibrium-limited reactions.

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ARTICLE

Journal of Materials Chemistry A

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Graphical abstract