Simultaneous enhancement of mechanical properties and CO₂ selectivity of ZIF-8 mixed matrix membranes: interfacial toughening effect of ionic liquid

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Abstract

Fine-tuning of interfacial adhesion between fillers and polymer matrices is crucial to the separation performance of mixed matrix membranes (MMMs) and their mechanical properties. Direct incorporation of metal organic framework (MOF) particles in polymers often leads to insufficient adhesion and non-selective interfacial voids. Herein, we present a novel strategy to develop toughened MOF-polymer interface by confining a room temperature ionic liquid (IL) [bmim][Tf₂N] into ZIF-8 cages. The diffusion of the IL out of the IL-incorporated ZIF-8 (IL@ZIF-8) was restrained by a water-washing process, confirmed by energy-dispersive X-ray spectra. Scanning electron microscopy images and differential scanning calorimetry measurements verified the interfacial toughening between the polymer and the IL@ZIF-8 filler. As a result, the mechanical properties and gas separation performance of IL@ZIF-8/Pebax membranes were significantly improved at the same time. The maximum tensile strength and elongation at break of IL@ZIF-8/Pebax membranes, obtained at a loading of 15 wt%, were 20% and 280% higher than those of pure Pebax membrane, respectively. Moreover, IL@ZIF-8/Pebax membranes showed improved molecular sieving properties compared to ZIF-8/Pebax membranes, due to a stiffer interphase between the filler and the polymer and a reduction in the effective aperture size of ZIF-8. The MMM with 15 wt% IL@ZIF-8 has a substantial improvement in both CO₂ permeability (increased by 45%) and selectivity (increased by 74% for CO₂/N₂ and 92% for CO₂/CH₄) over pure Pebax membrane. The presented strategy of fabricating IL@MOF/polymer membranes with desired interfacial structures can be conveniently expanded to a wide range of material combinations.

Keywords:

Interfacial toughening; Mixed matrix membranes; Ionic liquid; Mechanical stability; Gas separations

1. Introduction

CO₂ capture and storage is receiving tremendous attention around the world for both environmental and energy reasons. In particular, advanced separation technologies with improved energy efficiency are urgently demanded for separating CO₂ from flue gas (CO₂/N₂) and natural gas (CO₂/CH₄). One such technology is membrane-based separation, which is very promising due to its high efficiency, simple process design/operation, and small carbon footprint [1]. To further improve the gas separation performance of commercial polymer membranes, researchers came up with the concept of mixed matrix membranes (MMMs) comprising of porous fillers and polymer matrices, which can combine the excellent transport performance of the fillers with good processibility of the polymers [2-5].

The transport and mechanical properties of MMMs, as with any other composite materials, are strongly dependent on the nanoscale structures of the filler-polymer interfaces [2]. The poor compatibility between filler particles and polymers will result in voids at the interface of the two phases, for example the frequently observed “sieve in a cage” morphology in zeolite/glassy polymer MMMs [6]. The interfacial voids would severely undermine the gas permeation selectivity of MMMs. Moreover, the discontinuity between the two phases would lead to a loss of mechanical properties of the MMMs, especially at high loadings, which reduces the processibility of MMMs. Therefore, it is of critical importance to obtain desired filler-polymer interfacial structures for MMMs.

Recently, metal-organic frameworks (MOFs), a family of porous crystalline frameworks, have shown superior performance as attractive fillers of MMMs, owing to their tunable functionalities, high porosity, and convenient synthesis [7-9]. Although the inorganic-organic hybrid nature of MOFs usually results in improved compatibility with polymers, as compared to zeolites and carbon molecular sieves, further improvement of the adhesion between the polymer matrices and the fillers is greatly desired. To improve the filler-polymer interaction, various modification techniques for the fillers have been developed in the past few years, including priming [10], use of silane coupling agents [11], particle fusion [12], and functionalization of MOF linkers [13-15]. However, it is still challenging to obtain a desired interfacial morphology and improve the gas separation and mechanical properties of MMMs.

Ionic liquids (ILs) have been used as gas separation membrane materials for years, owing to their selective adsorption of different gases [16-18]. In addition to blending ILs with polymer directly, free ILs have also been incorporated with polymers and MOFs (or zeolites) to form IL/filler/polymer MMMs and enhanced the permeability of resulting membranes greatly [19-22]. Hudiono et al. demonstrated that ILs can behave like a wetting agent in zeolite/polymer MMMs and improve the compatibility between zeolite and polymer [19, 20]. Hao et al. prepared IL/ZIF-8/poly(ionic liquid) mixed matrix membranes and demonstrated that the introduction of ZIF-8 considerably improved gas permeability without compromising CO₂/N₂ and CO₂/CH₄ selectivities, indicating the absence of defects in the MMMs [21]. In a similar approach,

Casado-Coterillo et al. prepared [emim][Ac]/MOF/chitosan mixed matrix membranes using nanometer-sized ZIF-8 and HKUST-1 particles, with a maximum CO₂ permeability of over 5000 Barrer [22]. In these works, free ILs acted like lubricants between the fillers and the polymer matrices, leading to good compatibility in the three-component MMMs and high CO₂ permeability of the MMMs. However, the introduction of ILs in these systems had hardly improve the CO₂ selectivity of resulting MMMs.

Instead of dispersing free ILs and MOFs directly in polymer matrix, we propose to incorporate ILs in MOFs to enhance the interfacial compatibility between MOF fillers and the polymer matrix, as shown in Scheme 1. Our hypothesis is that the ILs embedded in the outer surface of MOF fillers could act as sealants between the filler and polymer phases. Consequently, both mechanical and gas separation properties of resulting MMMs could be enhanced. Moreover, the available pore volumes and aperture size of MOF fillers will be reduced by the presence of ILs in MOFs, which may further improve the molecular sieving properties of the resulting MMMs.

Scheme 1 Structures of MMMs with IL and porous fillers: (a) free IL dispersed in filler/polymer matrix (b) IL confined in porous MOF fillers.

It should be noted that while we were preparing this manuscript a very recent paper by Ban et al. implemented a similar idea of using IL-incorporated MOFs as fillers of mixed matrix membranes [23], showing enhanced molecular sieving properties of MMMs due to the presence of IL in MOF. However, there is one major important difference between our strategy and the reported one: IL was mainly distributed at the filler-polymer interface in our membranes while IL was confined in the pores of fillers in theirs.

In the present work, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), an ionic liquid with high CO₂ solubility, was used as a guest material. ZIF-8, consisting of zinc and 2-methylimidazolate with SOD topology, was chosen as a model of host material due to its ultra-microporosity and relatively high thermal and chemical stability. Pebax, a highly permeable polyether-polyamide copolymer, was used as the matrix polymer of the MMMs. Their structures are presented in Fig. 1.

Pebax 1657

[bmim][Tf₂N]

ZIF-8

Fig. 1. Chemical structures of Pebax 1657, [bmim][Tf₂N], and ZIF-8.

The effect of IL incorporation on the surface and adsorption properties of ZIF-8 were investigated by a multitude of characterization methods e.g. PXRD, FTIR, N₂ adsorption, etc. The loading of [bmim][Tf₂N] in IL-incorporated ZIF-8 (denoted as IL@ZIF-8) were calculated from elemental analysis and TGA. Then, IL@ZIF-8/Pebax MMMs with different filler loadings were made via solution-casting method. The toughening effect of ILs at the filler-polymer interface was studied by measurements of both mechanical and thermal properties of MMMs. Finally, the permeabilities of pure CO₂, N₂, CH₄ and H₂ through these MMMs were measured and compared with the state-of-the-art data using Robeson plot. The improvement in CO₂/N₂ and CO₂/CH₄ separation performance confirmed the enhanced molecular sieving property of obtained membranes.

2. Experimental

2.1 Materials

Pebax 1657 pellets was supplied by Arkema (France). Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$) were obtained from Sinopharm (China) and Guangfu Fine Chemicals (China), respectively. 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) was purchased from Chengjie Chemicals (China). Methanol and ethanol were purchased from Damao Fine Chemicals (China). CO_2 , N_2 , CH_4 and H_2 were supplied by Dalian Institute of Chemistry and Physics (China). All chemicals were of reagent grade and used as received. Deionized water was used in all the experiments.

2.2 Membrane preparation

2.2.1 Synthesis of ZIF-8 particles

ZIF-8 was synthesized using a reported recipe at room temperature [24]. 0.744 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 12.3 g 2-methylimidazole were dissolved in 10 and 90 ml water, respectively. The zinc nitrate solution was then mixed with the ligand solution under stirring. Sixty minutes later, the product was collected by centrifuging and washed with methanol three times. After drying in the air, the product was activated in a vacuum oven at 150 °C overnight.

2.2.2 Synthesis of IL@ZIF-8 particles

IL@ZIF-8 was prepared by soaking activated ZIF-8 in a methanol solution of [bmim][Tf₂N]. The amount of ZIF-8 was determined by equation (1) (see 2.2.3) and in the range of 0.117-0.110 g, while the amount of IL and methanol were fixed at 0.5 g and 10 ml respectively. Excessive amount of IL was used to make sure the IL contents in the different batches of IL@ZIF-8 were at the same level. The soaking of ZIF-8 in the IL solution was conducted in a sonication bath for 2 h at 50 °C. IL@ZIF-8 were collected by centrifuging and washed with water two times (5 minutes each time) at 10 °C. IL@ZIF-8 were further dried in a vacuum oven at 100 °C overnight for characterization use. While for the preparation of MMMs, they were dispersed in 3 ml water and then mixed with polymer solution without any drying.

2.2.3 Membrane preparation

Pebax pellets were mixed with H_2O /ethanol (30/70 by weight) to give a 3 wt% solution. The polymer was dissolved after two hours by refluxing the mixture at 80 °C.

An amount of ZIF-8 (or IL@ZIF-8), defined by equation (1), was dispersed in 3 ml ethanol (H_2O for IL@ZIF-8), and mixed with 11g of the polymer solution followed by stirring for 10 min. The resulting mixture was sonicated for 30 min to degas and then cast on a flat-bottom Petri dish. Thereafter, the solvent was evaporated at 50 °C for 12 h. The nascent membranes were removed carefully from the Petri dish and further dried for 12 h at 50 °C under vacuum. The average thickness of MMMs was in the range of 70-90 μm , measured with a digital micrometer (IP65, Mitutoyo). For comparison, pure Pebax membrane and IL/Pebax blend membranes were also prepared in a similar procedure.

$$\text{MOF loading (wt\%)} = \left(\frac{\text{MOF wt}}{\text{MOF wt} + \text{Pebax wt}} \right) \times 100\% \quad (1)$$

2.3 Characterization techniques

SEM images of ZIF-8 crystals and MMMs were recorded on a Quanta 450 (FEI Co., USA). All specimens were vacuum sputtered with gold for 90 s prior to characterization. EDX measurement was conducted by an Oxford X-max detector.

XRD patterns of ZIF-8 and IL@ZIF-8 particles were collected on a Rigaku D/Max-2400 X using a Cu K source. The diffraction was operated at 40 kV and 100 mA at a scanning speed of 6°/min in the 2θ range of 5-30°.

The FTIR spectra of [bmim][Tf₂N], ZIF-8, and IL@ZIF-8 particles were recorded on a Nexus FTIR spectrometer (Thermo Nicolet, USA) with anhydrous KBr as the dispersing agent.

Nitrogen adsorption-desorption measurements of the ZIF-8 and IL@ZIF-8 particles were conducted on an ASAP2010 (Micromeritics, USA) apparatus at 77 K. The internal surface area was calculated by the BET method. The micropore volume was determined by the t-plot method. The pore size distribution was determined by non-local density functional theory (NLDFT) method.

Thermogravimetric analysis (TGA) was performed using a TGA Q50 (TA Instruments, USA). Each time, approximately 5 mg well-dried sample was accurately weighed before being calcinated under high-purity N₂ flowing in the in-built platinum pan of the TGA instrument. The samples were programmed to be heated from 50 to 850 °C at a heating rate of 10 °C min⁻¹.

Thermal properties, i.e., glass transition temperature (T_g) and melting point (T_m), of the MMMs were calculated from differential scanning calorimetry (DSC) measurements, which were performed using a TGA Q20 (TA Instruments, USA). For DSC measurements, samples were hermetically sealed into aluminum pans. The samples were first heated to 230 °C, then cooled to -70 °C, and then heated to 230 °C again. The scan rate was fixed at 10 °C min⁻¹. For each membrane, a minimum of three samples were measured to ensure the reproducibility of the experimental results.

The surface zeta potentials of the ZIF-8 and IL@ZIF-8 particles in water and ethanol were measured using a Malvern Zetasizer Nano-ZS90 System. Samples were slowly injected into the zeta potential cell to avoid any interference by bubbles.

The tensile stress-strain characteristics of membranes were studied using a testing machine (CMT8502, Shenzhen SANS Testing Machine Co. Ltd, China) with an operating head load of 5 KN. The testing speed was set at a rate of 10 mm min⁻¹. All samples were prepared with a width of 5 mm and a length of 30 mm. Each test was repeated three times.

2.4 Gas permeation measurements

The pure gas permeability of CO₂, H₂, N₂, and CH₄ were determined by the constant-volume method, which measures the steady-state gas flux through a membrane under a given pressure difference. All permeation data were determined at 25 °C and the feed pressure was 1 bar. For

each membrane, a minimum of three samples were measured to ensure the reproducibility of the experimental results.

The gas permeability was determined using the following equation:

$$P = \frac{273}{76} \frac{VL}{ATp_0} \frac{dp(t)}{dt} \times 10^{10} \quad (2)$$

where P is the permeability coefficient of a membrane to a certain gas and its unit is Barrer (1 Barrer = $10^{-10} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), V the volume of the low-pressure chamber (cm^3), A the effective area of the membrane (cm^2), L the thickness of the membrane (cm), p_0 the pressure of the feed gas in the upstream chamber (cmHg), T the temperature of the measurement (K), and $dp(t)/dt$ the slope of pressure increase measured by a pressure transducer in the low-pressure chamber (cmHg s^{-1}).

The diffusivity coefficient (D) and solubility coefficient (S) are obtained from equation (3) and equation (4), respectively:

$$D = \frac{L^2}{6\theta} \quad (3)$$

$$S = \frac{P}{D} \quad (4)$$

where θ is the lag time.

The ideal selectivity is defined as the permeability ratio of two types of gas as equation (5):

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \times \left(\frac{S_A}{S_B} \right) \quad (5)$$

where P_A and P_B are permeability of gas A and gas B respectively. (D_A/D_B) is diffusivity selectivity and (S_A/S_B) is solubility selectivity.

3. Results and discussion

3.1 Incorporation of [bmim][Tf₂N] in ZIF-8

The synthesized ZIF-8 particles were characterized by SEM and shown in Fig. 2. The average particle size was estimated to be in the range of 200-350 nm. IL@ZIF-8 was prepared by soaking activated ZIF-8 particles in the methanol solution of [bmim][Tf₂N]. The introduction of IL into ZIF-8 was conducted with the help of a solvent, rather than a direct mixing of these two components as previously reported [25] or in-situ incorporation of IL into ZIF-8 via ionothermal synthesis [23], to avoid an excessive occupation of IL in ZIF-8 cavities, which might block all gas molecules and hence decrease the separation performance of corresponding MMMs.

Fig. 2. SEM image of ZIF-8 particles.

Successful introduction of [bmim][Tf₂N] in ZIF-8 framework was confirmed by powder X-ray diffraction, FTIR and N₂ adsorption measurements. As shown in Fig. 3, the crystal structure of ZIF-8 was remained after the incorporation of [bmim][Tf₂N]. The intensity of the (011) peak notably decreased, implying a change in electron density inside the ZIF-8 pores. This phenomenon was also observed in IL@ZIF-8 materials prepared by direct soaking [25] and in-situ synthesis [23].

Fig. 3. XRD patterns of ZIF-8 and IL@ZIF-8 particles.

Fig. 4 shows FTIR spectra of ZIF-8, [bmim][Tf₂N], and IL@ZIF-8. For the spectrum of IL@ZIF-8, new peaks appeared around 1065, 1188, 1225 and 1347 cm⁻¹, that are assigned to the vibrations of the [Tf₂N](-) anion, indicating a successful incorporation of [bmim][Tf₂N] in the ZIF-8 frameworks. In particular, the blue shift of S-N-S stretching band (from 1055 to 1065 cm⁻¹) in IL@ZIF-8 compared to bulk [bmim][Tf₂N] suggests a strong interaction of [Tf₂N](-) anion with the zinc nodes of ZIF-8 [23].

Fig. 4. FTIR spectra of [bmim][Tf₂N], ZIF-8, and IL@ZIF-8.

N₂ adsorption measurements (Fig. 5) shows that both ZIF-8 and IL@ZIF-8 exhibit type-I adsorption behavior, suggesting that the introduction of IL did not affect the microporous nature

of ZIF-8. After IL incorporation, the BET surface area and pore volume decreased from 1029 m² g⁻¹ and 0.60 cm³ g⁻¹ for ZIF-8 to 698 m² g⁻¹ and 0.43 cm³ g⁻¹ for IL@ZIF-8. About 30% of ZIF-8 pore volume was occupied by the IL and the pore diameter was reduced accordingly. Compared to IL@ZIF-8 prepared by in-situ synthesis (60% of pore volume was occupied [23]), the loading of IL into ZIF-8 in our work is much smaller, which can be explained by the occupation and subsequent evacuation of the solvent.

Fig. 5. N₂ adsorption/desorption isotherm (a) and pore size distribution (b) of ZIF-8 and IL@ZIF-8.

C, H, and N elemental analysis and TGA measurements were performed to quantify the amount of IL loadings in IL@ZIF-8 composites. The IL contents of IL@ZIF-8 prepared from different ZIF-8/[bmim][Tf₂N] ratios were calculated from the result of elemental analysis and were in the range of 16.8-18.3 wt%. The loading of IL in IL@ZIF-8 composite measured from TGA results (Fig.6) is 16.5 wt%, which coincides with the results from elemental analysis. The weight loss of IL@ZIF-8 around 450 °C indicates the presence of [bmim][Tf₂N]. Both the decomposition temperature of the IL and ZIF-8 in IL@ZIF-8 were slightly brought forward, presumably owing to a strong interaction between the IL and ZIF-8.

Fig. 6. TGA (a) and DTG (b) curves of the IL, ZIF-8 and IL@ZIF-8 particles.

3.2 Water-confining of [bmim][Tf₂N] in ZIF-8 cages

IL@ZIF-8 particles were washed with water before dispersed in polymer solution to prevent the leakage of IL from ZIF-8 cavities. This is because if the majority of ILs diffuse into the polymer matrix, the resulting membrane structure would be IL/ZIF-8/polymer rather than IL@ZIF-8/polymer.

Water was used to confine the diffusion of the IL as [bmim][Tf₂N] is hydrophobic and not soluble in water. The EDX measurements of MMMs with washed and unwashed IL@ZIF-8 particles were displayed in Fig. 7. The intensity of F indicates the content of [bmim][Tf₂N] in the membrane matrix and Zn for ZIF-8. The Zn/F ratio (by weight) for MMMs with water-washed IL@ZIF-8 and unwashed IL@ZIF-8 were 13.7 and 2.0, respectively, indicating that the amount of IL in IL@ZIF-8 that diffused into polymer matrix during membrane formation was significantly decreased by the water-washing process.

Fig. 7. EDX measurements of MMMs with water-washed and unwashed IL@ZIF-8. The Au peak was attributed to sputtered gold used for SEM characterization. The S peak (around 2.5 keV) was not shown here because it overlapped with an Au peak.

3.3 Morphology of mixed matrix membranes

Surface zeta potential measurements of ZIF-8 and IL@ZIF-8 particles provide further insight into the dispersibility of the fillers in the solvents used for membrane preparation. The higher the zeta potential is, the more stable the particles are. As shown in Table 1, ZIF-8 particles can be readily dispersed in water since the external surface of ZIF-8 is rather hydrophilic, although the internal surface of ZIF-8 is hydrophobic. IL@ZIF-8 particles, on the contrary, have poor dispersibility in water because of the residual [bmim][Tf₂N] on the external surface of ZIF-8. But both fillers have similar dispersibility in ethanol.

Nevertheless, both the ZIF-8 and IL@ZIF-8 particles could be uniformly dispersed in the Pebax solution with water-ethanol binary solvent and no precipitation was observed during the

whole process. Surface and cross-section SEM images of MMMs (Fig. 8 and 9) shows that there is no defect or agglomerate in any sample, indicating excellent adhesion between the polymer and fillers.

Table. 1 Surface zeta potentials of ZIF-8 and IL@ZIF-8 in water and ethanol.

Sample	Zeta potential / mV	
	Water	Ethanol
ZIF-8	23.2	13.5
IL@ZIF-8	3.3	11.8

However, obvious differences in membrane morphology of the two kinds of membranes can also be observed from the cross-section SEM images. Taking the membranes with the filler loading of 15 wt% as an example, clear spherulitic structure and polymer veins are observed for ZIF-8/Pebax membranes (Fig. 8f), while the polymer phase is more homogeneous in IL@ZIF-8/Pebax membranes (Fig. 9d). Since Pebax is composed of soft, hydrophilic polyether (PE) blocks and rigid, hydrophobic polyamide (PA) blocks, it can be concluded that the micrometer-scale phase separation between the PA and PE blocks was remained with the incorporation of ZIF-8 particles, while a well interpenetrated network between PA and PE blocks was formed with the incorporation of IL@ZIF-8 particles.

It seems that the ILs incorporated on ZIF-8 greatly influenced the formation of interface between IL@ZIF-8 fillers and the polymer. To investigate the effects of different filler-polymer interfaces on the overall performance of membranes, mechanical and gas permeation properties of membranes were studied.

Fig. 8. Surface (a, c, e, g) and cross-section (b, d, f, h) SEM images of pure Pebax (a, b) and ZIF-8/Pebax membranes with 5 wt% (c, d), 15 wt% (e, f), and 25 wt% (g, h) filler loadings.

Fig. 9. Surface (a, c, e) and cross-section (b, d, f) SEM images of IL@ZIF-8/Pebax membranes with 5 wt% (a, b), 15 wt% (c, d), and 25 wt% (e, f) filler loadings.

3.4 Mechanical properties of IL@ZIF-8/Pebax membranes

The tensile strength and elongation at break of pure Pebax, ZIF-8/Pebax, [bmim][Tf₂N]/Pebax, and IL@ZIF-8/Pebax membranes were summarized in Fig. 10. The mechanical strength of

[bmim][Tf₂N]/Pebax membranes were impaired obviously. The mechanical strength of the Pebax matrix was mainly provided by the rigid hydrophobic PA blocks, while elongation by soft hydrophilic PE blocks. For [bmim][Tf₂N]/Pebax membranes, the hydrophobic IL, acting as a plasticizer, softens the rigid PA blocks of the polymer matrix and thus lowers the tensile strength of the blend membranes [26].

However, it is noteworthy that ZIF-8 and IL@ZIF-8 particles had inverse effects on the mechanical properties of corresponding MMMs. The tensile strength of ZIF-8/Pebax membranes decreased continuously with increased ZIF-8 content while their elongation decreased at low loading (< 10 wt%) and then increased at higher loading. On the contrary, both the tensile strength and elongation of IL@ZIF-8/Pebax membranes increased with the increase in IL@ZIF-8 loading, up to 15 wt%. The maximum tensile strength and elongation of IL@ZIF-8/Pebax membranes, obtained at 15 wt% loading, were 12.2 MPa and 750%, which were 20% and 280% higher than those of pure Pebax membrane, respectively.

Fig. 10. Tensile strength (a) and elongation at break (b) of membranes with different fillers or additives.

Studies on the failure of particle-reinforced polymer composites have indicated that, when the interphase is stiffer than the surrounding matrix, there is a less tendency for cracks to develop in this region. On the other hand, when the surface chemistry of the particles leads to a softening of the surrounding matrix, the probability of cracks/debonding developing in the interphase region increases [27, 28]. Therefore, it can be concluded that the filler-polymer interfacial structures in IL@ZIF-8/Pebax membranes are tougher/stiffer than those in ZIF-8/Pebax membranes.

To illustrate the toughening effect of IL@ZIF-8 fillers, a mechanism of the formation of filler-polymer interfaces was proposed in Scheme 2.

Scheme 2 Hypothetical mechanism of the toughening of filler-polymer interface: (a) the preferential adsorption of PA block on IL@ZIF-8 and (b) the aggregation of [bmim][Tf₂N] at the filler-polymer interface.

In the membrane formation process, the PA blocks would assemble preferentially around the hydrophobic sites of IL@ZIF-8 particles owing to their hydrophobic-hydrophobic interaction. Hereafter, as the membrane had become nearly solidified, the solvent (methanol here) were still diffusing out of the ZIF-8 framework and dragging the IL to the interfaces between fillers and polymers. As a result, the bulkier IL clusters, which themselves have high compatibility with the polymer, were embedded in the apertures of ZIF-8 and could act as cross-linking agents between the two phases. The improved mechanical strength of IL@ZIF-8/Pebax membranes should be attributed to the strong interaction between IL@ZIF-8 particles and the PA domains while the increased elongation was a result of the well interpenetrated network between PA and PE blocks.

Nevertheless, in the case of ZIF-8/Pebax membranes, the packing of polymer chains was hardly affected. The ZIF-8 fillers would be mainly wrapped by the soft PE blocks due to a lack of strong interactions between the rigid PA blocks and the fillers. Therefore, the tensile strength of ZIF-8/Pebax membranes was weakened and the elongation of ZIF-8/Pebax membranes was slightly increased by the addition of ZIF-8.

This hypothesis was verified by DSC measurements of these two kinds of mixed matrix membranes. As shown in Table 2, the melting point of PA segment was not influenced by the incorporation of the ZIF-8, while the melting point of both PA and PE segments were slightly decreased by the incorporation of IL@ZIF-8. The reduction in melting point of PA segment suggests the IL@ZIF-8 enhanced the miscibility between PA and PE segments in the membrane formation process. It also can be seen that the increase in T_g of IL@ZIF-8/Pebax membranes is higher than that of ZIF-8/Pebax membranes, suggesting the IL@ZIF-8 had a stronger effect on the packing of polymer chains than ZIF-8.

Both the tensile strength and elongation of IL@ZIF-8/Pebax membranes decreased when the loading of IL@ZIF-8 was over 15 wt%, presumably owing to the fact that the volume fraction of ZIF-8 particles had reached the threshold, which can be concluded from the SEM images. When the filler loading reaches the threshold, filler-filler interface rather than filler-polymer interface would dominate the properties of the MMMs [29]. Since voids would be formed easily at the

filler-filler interface without the presence of a polymer phase, the decrease of tensile strength and elongation of the MMMs with increasing filler loading can be predicted.

Table 2 Thermal properties of the ZIF-8/Pebax and IL@ZIF-8/Pebax membranes.

Membrane	Filler loading [wt%]	T_g [°C]	T_m (PE) [°C]	T_m (PA) [°C]
Pebax	0	-52.5 ± 1.2	12.5 ± 0.1	204.4 ± 0.1
ZIF-8/Pebax	5	-51.8 ± 1.3	11.9 ± 0.1	205.1 ± 0.2
	10	-50.4 ± 0.9	11.6 ± 0.1	204.4 ± 0.1
	15	-49.2 ± 1.1	11.8 ± 0.3	204.9 ± 0.1
	20	-46.0 ± 0.4	10.8 ± 0.2	204.2 ± 0.1
	25	-46.3 ± 0.5	11.7 ± 0.1	204.3 ± 0.2
IL@ZIF-8/Pebax	5	-50.5 ± 0.7	11.2 ± 0.1	202.9 ± 0.1
	10	-47.7 ± 1.0	11.4 ± 0.2	202.8 ± 0.1
	15	-46.4 ± 1.3	10.9 ± 0.3	202.6 ± 0.3
	20	-43.1 ± 0.5	11.0 ± 0.4	203.3 ± 0.1
	25	-39.2 ± 0.8	12.1 ± 0.1	203.9 ± 0.3

It should be noted that tensile strength and elongation at break, which represent the toughness and ductility of materials respectively, are rarely increased at the same time for MMMs, to the best of our knowledge. Therefore, this IL-incorporation method proposed in this work may provide an efficient strategy for improving the mechanical compatibility between porous fillers and polymers in MMMs.

3.5 Gas separation performance

The gas separation performance of the MMMs with different ZIF-8 and IL@ZIF-8 loadings are displayed in Fig. 11. For ZIF-8/Pebax membranes, the permeabilities of all gases increased while the CO₂/N₂ and CO₂/CH₄ selectivities decreased slightly, with the increase in ZIF-8 loading. The enhancement in gas permeabilities is attributed to the high porosity and flexible framework of the ZIF-8. Although the crystallographically-determined aperture size of ZIF-8 is 3.4 Å, just in between the kinetic diameter of CO₂ (3.3 Å) and N₂ (3.64 Å), ZIF-8 has only insignificant molecular sieving ability towards CO₂ over N₂ and CH₄ (3.8 Å), which has been proved in the previous works [30, 31]. This phenomenon is mainly due to the fact that the effective aperture size of ZIF-8 is ~ 4.0 Å, much larger than the crystallographically-determined aperture size due to the flopping motion of the ligand [32].

Fig. 11. Pure gas permeabilities (a) and CO₂/N₂ and CO₂/CH₄ selectivities (b) of MMMs with different ZIF-8 or IL@ZIF-8 loadings.

In contrast, for IL@ZIF-8/Pebax membranes, the permeabilities of N₂ and CH₄ decreased as the filler loading increased from 0 to 15 wt%, while the CO₂ permeability increased continuously. Accordingly the CO₂ selectivities increased significantly in the 0 to 15 wt% range of IL@ZIF-8 loading, from 48.2 to 83.9 for CO₂/N₂ and from 18.1 to 34.8 for CO₂/CH₄, implying a molecular sieving effect of IL@ZIF-8. To further confirm this, we measured H₂ (2.89 Å) permeability of IL@ZIF-8 MMMs (Fig. 12) and found that the permeation of H₂ showed similar trend to that of CO₂.

Fig.12 Pure gas permeabilities (a) and CO₂/H₂ selectivity (b) of MMMs with different ZIF-8 or IL@ZIF-8 loadings.

Normalized permeabilities of all gases, as a function of IL@ZIF-8 loading, were presented in Fig. 13. The data were normalized on the data of pure Pebax membranes. H₂ and CO₂, with smaller kinetic diameters, showed enhanced permeability when the loading of IL@ZIF-8 increased from 5% to 15%. N₂ and CH₄, on the contrary, showed reduced permeability in the same range of filler loadings. Therefore, we can conclude that IL@ZIF-8 has improved the molecular sieving properties of Pebax membranes.

Fig. 13 Normalized gas permeabilities of IL@ZIF-8/Pebax membranes with 5, 10, and 15 wt% filler loadings.

Detailed analysis on gas diffusivity and solubility coefficients of IL@ZIF-8/Pebax membranes were summarized in Table 3 and Table 4. For loadings up to 15 wt%, the addition of IL@ZIF-8 produced a simultaneous enhancement of both diffusivity and solubility coefficients of CO₂. With

the filler loading was increased from 0 to 15 wt%, the diffusivities of CO₂ and H₂ were increased substantially while the counterparts of N₂ and CH₄ were decreased, indicating the increase in CO₂ selectivity was mainly due to the improvement in diffusivity selectivity for CO₂ over gases with larger kinetic diameters. The improvement in diffusivity selectivity for CO₂ can be attributed to a stiffer interphase between ZIF-8 and the polymer matrix, as illustrated in Scheme 1. The increase in diffusivity selectivity was also observed by other researchers aiming to develop strong filler-polymer interactions in MMMs [12].

Table 3 Gas diffusivity coefficients and solubility coefficients of IL@ZIF-8/Pebax membranes.

IL@ZIF-8 loading (wt%)	$D_{CO_2}^a$	$S_{CO_2}^b$	$D_{H_2}^a$	$S_{H_2}^b$	$D_{CH_4}^a$	$S_{CH_4}^b$	$D_{N_2}^a$	$S_{N_2}^b$
0	9.23	7.86	73.10	0.09	3.02	1.33	3.61	0.42
5	10.22	8.04	79.25	0.10	2.76	1.41	3.33	0.43
10	11.48	8.27	88.34	0.11	2.45	1.48	2.95	0.45
15	12.80	8.19	102.45	0.10	2.20	1.37	2.67	0.47
20	18.32	7.50	136.66	0.10	4.50	1.22	4.90	0.50
25	25.65	6.59	165.87	0.10	7.69	0.96	6.82	0.53

^a Diffusivity coefficient [cm^2/s] $\times 10^7$ ^b Solubility coefficient [cm^3 (STP)/ cm^3 cmHg] $\times 10^3$

Table 4 Diffusivity selectivities and solubility selectivities of IL@ZIF-8/Pebax membranes.

IL@ZIF-8 loading (wt%)	D_{CO_2}/D_{N_2}	S_{CO_2}/S_{N_2}	D_{CO_2}/D_{CH_4}	S_{CO_2}/S_{CH_4}	D_{CO_2}/D_{H_2}	S_{CO_2}/S_{H_2}
0	2.56	18.87	3.07	5.90	0.13	85.29
5	3.09	18.84	3.70	5.72	0.13	77.05
10	3.90	18.47	4.69	5.58	0.13	74.09
15	4.79	17.50	5.82	5.99	0.13	78.56
20	3.73	14.94	4.07	6.16	0.13	77.82
25	3.76	12.55	3.32	6.89	0.15	64.74

Comparing Fig. 10 and Fig. 11, it can be seen that all of the four properties (tensile strength, elongation, permeability, and selectivity) of the IL@ZIF-8/Pebax membranes, with the increasing filler loading, increase first, reach maximum values at the loading of 15 wt%, then decrease. The similar effects of IL@ZIF-8 on the mechanical and gas permeation properties of the MMMs indicates that the improved filler-polymer interface plays a major role in enhancing the performance of the MMMs. Moreover, a reduction in the effective aperture size of ZIF-8 possibly

resulting from the hindrance of the flopping motion of the ligand owing to the presence of the ILs, may also contribute to the enhancement in diffusivity selectivity for CO₂.

Similar to the observation in mechanical properties of the MMMs, the CO₂/N₂ and CO₂/CH₄ selectivities of IL@ZIF-8/Pebax membranes decreased when the loading of IL@ZIF-8 was over 15 wt%, implying the voids formed at the filler-filler interface when the volume fraction of fillers reached the threshold.

To better compare the effects of different additives on gas separation performance of membranes, [bmim][Tf₂N]/Pebax blend membranes were also prepared and their gas permeabilities were shown in Fig. 14. Although the addition of the IL significantly increased the permeability of CO₂ due to the plasticizer effect of the IL, the selectivity of CO₂ over other gases slightly decreased, which is consistent with similar work on other IL/polymer blend membranes [30].

Fig. 14. Gas separation performances of [bmim][Tf₂N]/Pebax blend membranes.

The differences in the separation performances of [bmim][Tf₂N]/Pebax blend membranes, ZIF-8/Pebax and IL@ZIF-8/Pebax membranes can be seen more clearly when plotted with the well-known Robeson upper bound (Fig. 15) [33]. It shows that [bmim][Tf₂N] and ZIF-8 particles can improve only the CO₂ permeability of membranes but lower the CO₂ selectivity when employed in membranes individually. In contrast, IL@ZIF-8 particles offer substantial improvement in both permeability (increased by 45%) and selectivity (increased by 74% for CO₂/N₂ and 92% for CO₂/CH₄) over pure Pebax membrane, with the potential to surpass the upper bound. Compared with other reported MOF-based MMMs and IL/polymer blend membranes (Table 5), the IL@ZIF-8/Pebax membranes prepared in this work showed higher selectivities with intermediate permeability, representing a well-balanced performance. The separation performance of IL@ZIF-8/Pebax membranes are lower than that of the other reported MMM based on

IL@ZIF-8 filler [23], which may be attributed to the differences in matrix polymer and testing conditions.

Fig. 15. CO₂/N₂ (a) and CO₂/CH₄ (b) separation performances of pure Pebax, ZIF-8/Pebax, IL@ZIF-8/Pebax, and [bmim][Tf₂N]/Pebax membranes in Robeson upper bound plot.

Table 5 Comparison of gas separation performances of this work with those of reported MMMs.

Membrane types —materials	P_{CO_2} (Barrer) ^a	$\alpha(\text{CO}_2/\text{N}_2)^a$	$\alpha(\text{CO}_2/\text{CH}_4)^a$	Testing conditions	Ref.
MOF/Polymer MMMs					
ZIF-8/PVC-g-POEM	623.0	—	11.2	35 °C, 1 bar	[34]
ZIF-90/PI	720	27 (37)	22	25 °C, 2 atm	[35]
Mg ₂ (dobdc)/PI	850	23	—	25 °C, 2 bar	[36]
NH ₂ -MIL-53/PI	58.5	—	36.6 (33.9)	35 °C, 150 psi	[37]
ZIF-8/Matrimid	25 ^b	—	52 ^b		[12]
ZIF-8-ambz-(30)/Matrimid	12 ^b	—	38 ^b	35 °C, 3.45 bar	[38]
Cd-6F/PI	37.8	35.1	44.8	25 °C, 2 atm	[39]
NH ₂ -MIL-53(Al)/PI	(15 ^b)	—	(36 ^b)	35 °C, 3 bar	[40]
ZIF-7/Pebax 1657	111	97	30	20 °C, 6.5 (2.75 for CO ₂) bar	[41]
ZIF-8/Pebax 2533	1287	32.3	9.0	RT, 2 bar	[42]
MIL-53(Al)/Matrimid	40	95.2	90.1	35 °C, 2bar	[43]
IL/Polymer blend membranes					
[emim][dca]/P([vbim][dca])	272.9 (253.5)	53.5 (50.6)	—	35 °C, 1-2 atm	[44]
[emim][B(CN) ₄]/P([vbim][dca])	340.1 (297.1)	42.0 (38.8)	—		
[bmim][CF ₃ SO ₃]/Pebax 1657	320 ^b	40 ^b	27 ^b	25 °C, 1 bar	[26]

[bmim][Tf ₂ N]/PI	501	27.6	14.5	35 °C, 75 cmHg	[45]
IL/Filler/Polymer MMMs					
[emim][Tf ₂ N]/SAPO-34/P(vinyl-IL)	527.2	26.0	24.9	23 °C, 1-1.5 atm	[20]
[emim][Tf ₂ N]/SAPO-34/P([SMIM][Tf ₂ N])	260	—	90	25 °C, 2 atm	[46]
[emim][B(CN) ₄]/ZIF-8/P[vbim][Tf ₂ N]	(906.4) (928.7)	(21.0) —	— (11.6)	35 °C, 3.5 bar	[21]
IL@MOF/Polymer MMMs					
[bmim][Tf ₂ N]@ZIF-8/PSF	(279) (253)	(130) —	— (45.7)	30 °C, 6 bar	[23]
[bmim][Tf ₂ N]@ZIF-8/Pebax 1657	104.9	83.9	34.8	25 °C, 1 bar	This work

^a The values in the bracket are for mixed-gas selectivity. ^b Values are approximated from plots.

4. Conclusions

In summary, we have provided a simple but effective strategy, i.e., ionic liquid incorporation, to enhance the interaction between the MOF filler and the polymer matrix in MOF-based MMMs. IL@ZIF-8 fillers were prepared by soaking activated ZIF-8 in [bmim][Tf₂N]/methanol solution, which can keep the required amount of IL to a minimum level. Water was used to restrain the leaking of hydrophobic [bmim][Tf₂N] out of the ZIF-8 cages, preventing the presence of free IL in the polymer phase. The interphase between IL@ZIF-8 and the polymer was toughened because of a strong hydrophobic-hydrophobic interaction between the filler and the polyamide block of the polymer.

As a result, the tensile strength and elongation of IL@ZIF-8/Pebax membranes increased simultaneously with the increased loading of IL@ZIF-8. The maximum tensile strength and elongation of IL@ZIF-8/Pebax membranes were 12.2 MPa and 750%, which were 20% and 280% higher than those of pure Pebax membrane, respectively. Moreover, IL@ZIF-8/Pebax membranes showed improved molecular sieving properties, due to the stiffer interphase between the filler and the polymer and the reduction in the effective aperture size of ZIF-8. The MMM with a loading of 15 wt% IL@ZIF-8 can increase the CO₂ permeability by 45%, CO₂/N₂ selectivity by 74%, and CO₂/CH₄ selectivity by 92%, respectively, compared with the pure polymer membrane.

The results demonstrate that IL@MOFs are promising fillers of MMMs for gas separation. As MOFs and ILs are both highly tunable, MMMs based on IL@MOFs could be elaborately designed to pursue advanced gas separation performance for various tasks.

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