

Stabilization of immiscible polymer blends using structure directing metal organic frameworks (MOFs)



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ABSTRACT

We have developed a novel approach for compatibilizing immiscible polymer blends using metal organic frameworks (MOFs). For the first time we demonstrated that the droplet diameter of the dispersed phase in a 1:1 immiscible polymer blend composed of 6FDA-DAM:DABA [copolymer of 4,4-hexafluoroisopropylidene diphthalic anhydride (6FDA), 2,4,6-trimethyl-1,3-phenylenediamine and 3,5-diaminobenzoic acid (DABA)], and polybenzimidazole (PBI), is dramatically reduced obtaining a uniform microstructure with the incorporation of as low as 5% (w/w) of the zeolitic imidazolate framework-8 (ZIF-8). This indicates a large improvement in the compatibility of the immiscible polymers with the inclusion of ZIF-8. As the ZIF-8 loading was further increased to 10% (w/w), the droplet diameter further decreased resulting in even higher compatibility. The compatibilizing effect can be attributed to a reduction in the interfacial energy of the immiscible polymers due to the interfacial localization of ZIF-8. This MOF based compatibilization of immiscible polymer blends can open up opportunities for the combination of different properties of polymers in membrane-based separations and in more applications.

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1. Introduction

The technology of polymer blends is one of the major areas of research and development in polymer science [1]. Blending of polymers leads to new materials that can synergistically combine the properties of polymers that are not achievable with individual components [2]. Moreover, it overcomes the need to synthesize new macromolecules for particular applications. However, due to the unfavorable entropy of mixing, most polymer blends tend to macroscopically phase separate [2]. In order to obtain complete miscibility, a favorable enthalpy of mixing is required, which can be achieved through specific interactions between polymers such as hydrogen bonding, dipole–dipole interactions or ion–dipole interactions [1,2]. In contrast, immiscible polymer blends are more common and have been used for a variety of applications including tires [3], organic light-emitting diodes [4], and sensors [5]. However, immiscible polymer blends are often characterized by

uncontrolled phase separation leading to inconsistent properties and poor mechanical stability [1]. Therefore, polymers in phase-separated blends have been commonly compatibilized with copolymers [6–8] and nanoparticles [9–13] to obtain uniform and stable morphologies [14–16]. The use of nanoparticles to stabilize immiscible polymer blends is more attractive since copolymers are difficult to synthesize and are specific to one polymer blend family [17]. Nanoparticle-compatibilized (NPC) immiscible polymer blends have afforded uniform and stable morphologies comprising both matrix-droplet and co-continuous morphologies [9].

Polyimides are an important class of polymers used in a variety of applications in fields such as fuel cells [18,19] gas separation membranes [20–23] and energy storage [24]. Furthermore, blends of polyimides are used for many applications due to their favorable properties such as toughness, high thermal stability, high temperature rigidity and good solvent resistance [1]. The co-polyimide 6FDA-DAM:DABA (3:2) (6FDD) (Fig. 1A) and PBI (Fig. 1B) are high performance polymers that have been used for membrane based separations [25–29]. Use of miscible polymer blends of polyimides/PBI has shown enhanced performances as compared to the individual polymers in the above applications [30,31]. However this approach is limited by the unavailability of many miscible polymer

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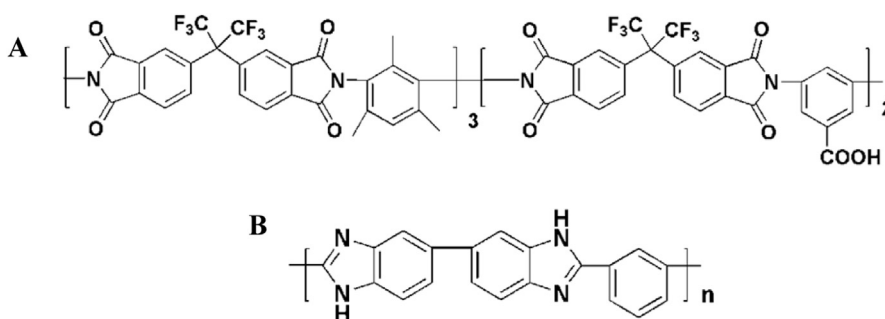


Fig. 1. The chemical structures of (A) 6FDA-DAM:DABA (3:2) and (B) PBI.

combinations. Therefore, it would be useful to explore the effect of immiscible polyimide/PBI blends in these and other applications. However, as the ultimate properties depend on the blend microstructure, the major challenge is to control the extensive phase separation as mentioned previously. Therefore the use of a compatibilizer is essential to obtain a uniform microstructure. Additionally, it could be beneficial to use a material that can potentially contribute toward enhancement of the properties of the resulting blend while improving the compatibility of the polymers. MOFs have been reported to improve separation performance of membranes due to their properties such as unique pore apertures, high surface area, chemical and thermal stability [32]. Furthermore, MOFs have been used in the field of catalysis, biomedical imaging, and proton, electron, and ion conduction [33]. To our knowledge the use of MOFs in NPC immiscible blends has not been previously reported. In this work, we describe the use of MOFs to stabilize an immiscible blend of two high performance polymers, 6FDD and PBI.

2. Experimental section

2.1. Materials

Anhydrous 1-methyl-2-pyrrolidone (NMP, 99.8% purity) was purchased from Sigma–Aldrich. Anhydrous dimethyl acetamide (DMAc, 99.8% purity) was purchased from EMD chemicals. 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, >99% purity) was purchased from Akron Polymer Systems Inc. and was dried under vacuum at 150 °C prior to use. 2,4,6-trimethyl-1,3-phenylenediamine (DAM, >97% purity) was purchased from TCI America and purified further by vacuum sublimation. 3,5-diaminobenzoic acid (DABA, 98% purity) was purchased from Sigma–Aldrich and was purified by recrystallization from water. Polybenzimidazole (PBI) S26 product was purchased from PBI Performance Inc. (26 wt.% in DMAc, 1.5% (w/w) LiCl, $M_w \sim 30,000$) and was used as received. Commercially available ZIF-8 (Basolite™ Z1200) was purchased from Sigma–Aldrich and was activated at 100 °C for 24 h under vacuum prior to use. Prior to use all solvents were dried over activated 4A molecular sieves purchased from Sigma–Aldrich.

2.2. Synthesis of 6FDA-DAM:DABA (6FDD, 3:2 molar ratio) polyimide

The synthesis of 6FDD (Fig. 2) was carried out using thermal imidization (in NMP) following a literature procedure [34]. The reaction was conducted under a nitrogen purge in a 100 mL three-neck flask equipped with a Dean Stark apparatus and a condenser. In the first step 2.000 g of 6FDA (4.502 m mol) in 8.5 mL of NMP were added dropwise to a solution of 0.274 g (1.808 m mol) DABA in 2.5 mL of NMP in a 100 mL three-neck flask (The monomer

concentration in the flask was kept at ~20 wt.%). The mixture was stirred for 1 h at room temperature. Then 0.406 g (2.70 m mol) of DAM monomer in 2.00 mL of NMP was added to the reaction flask and stirred at room temperature for 26 h to produce polyamic acid. Next, 1 mL of NMP and 5 mL of *o*-dichlorobenzene were added to the reaction mixture, which was then heated to 190 °C and maintained at this temperature with stirring for 30 h. Finally, the polymer solution was precipitated into 100 mL of 1:1 water:methanol, filtered, and washed with methanol. The resultant beige powder was dried under vacuum for 2 days at 120 °C. This method yielded 0.4 g of pale brown polymer (92% yield) with a M_w of 170,000 and PDI of 2.3.

2.3. Membrane fabrication

Separate solutions of 2% (w/w) PBI and 6FDD were prepared in DMAc by stirring at 80 °C for 24 h followed by filtering through 0.45 μm syringe filters. In the preparation of polymer blends, solutions of 6FDD were always added to PBI solutions. The total polymer concentration of the final polymer mixture solution was ~2% (w/w). To induce phase separation as well as to concentrate the blend solution, excess DMAc was evaporated by slowly purging with N_2 at 80 °C. The concentrated polymer solutions were then cast onto a glass substrate using a Sheen automatic applicator (1133N) equipped with a doctor blade. The membranes were initially dried using a heated casting table (50 °C for 12 h) under a N_2 flow. Finally, the membranes were peeled off from the glass substrate and annealed further under vacuum using a heating cycle of 80 °C for 24 h, 150 °C for 12 h, 200 °C for 12 h and 250 °C for 24 h, followed by cooling down to room temperature under vacuum.

The mixed-matrix membranes (MMM) were fabricated in the same way as the polymer blend membranes, but with the addition of a ZIF-8 dispersion. The weight ratios of 5% and 10% (w/w) [(weight of ZIF-8)/(total polymer weight)] ZIF-8 in DMAc were prepared separately and subjected to alternate stirring and sonication (15 min each) to ensure good dispersion. This cycle was repeated for 2 h and then 1/3 of the PBI solution was added to the dispersion. The resulting ZIF-8 polymer dispersion was stirred for 30 min and sonicated for another 30 min. This cycle was repeated twice and then the rest of the PBI was added and stirred at 80 °C for 12 h in a closed glass vial. After that the 6FDD polymer solution was added dropwise to the ZIF-8/PBI mixture and stirred further. Finally, excess DMAc was evaporated by the slow purging by N_2 at 80 °C. Casting, drying and annealing of the MMMs were performed using the same protocol as for the polymer blends.

2.4. Characterization

2.4.1. Characterization of 6FDD

The chemical structure of 6FDD was confirmed by ^1H NMR spectroscopy using a Bruker AVANCE III™ 500 NMR instrument.

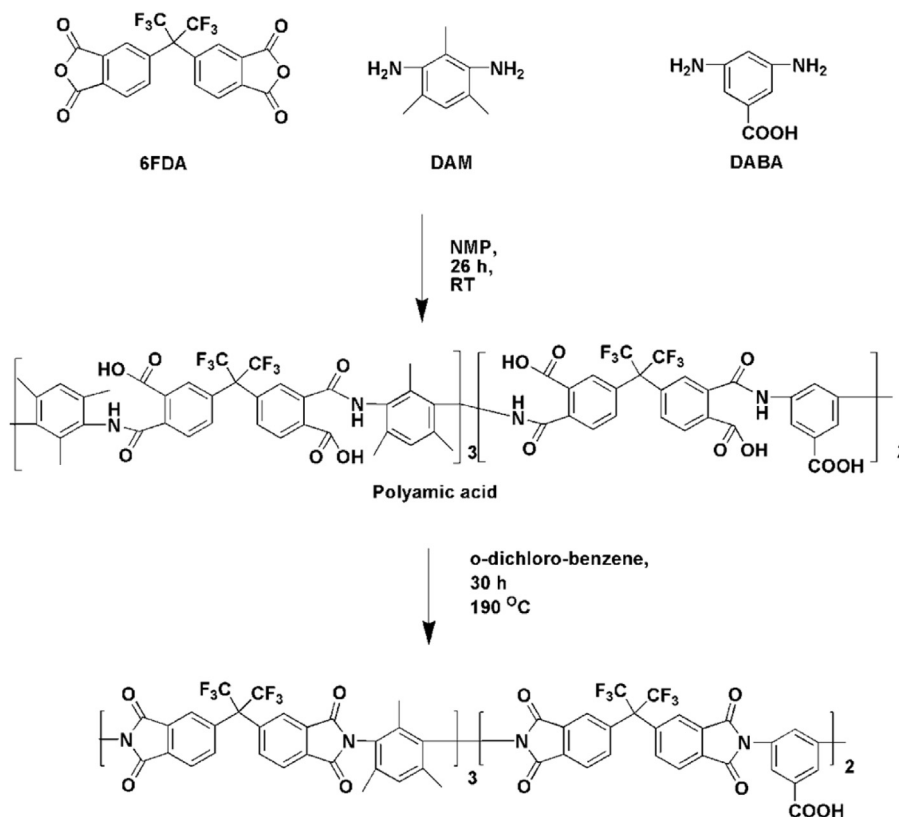


Fig. 2. Synthesis scheme of 6FDA-DAM:DABA (3:2) co-polyimide.

Samples were prepared in deuterated dimethyl sulfoxide with TMS as the internal standard. Molecular weight (M_w) was determined (M_w 170,000, PDI 2.3) on a gel permeation chromatography (Viscotek GPCmax, VE2001) system equipped with a Viscotek TDA 302 Triple Array Detector and two ViscoGEL I-Series (I-MBHMW 3078, Viscotek) columns in series. THF at a flow rate of 1 mL/min was used as the eluent, and polystyrene standards (Polymer Laboratories) were used for calibration. The chromatograms were analyzed using OmniSEC Software Version 4.6.

2.4.2. Characterization of membranes (SEM, TGA, FTIR, AFM, TEM)

Scanning electron microscope (SEM) images of membrane cross-sections were acquired using a Zeiss SUPRA[®]40 SEM with a field emission gun operating at 10 keV. Membrane cross-sections for SEM imaging were prepared by freeze-fracturing the samples after immersion in liquid nitrogen. These samples were coated prior to imaging using a Denton Vacuum Desk II sputter coater equipped with a gold/palladium target. The thicknesses of the membranes used in permeability studies were also measured by SEM. Thermogravimetric analysis (TGA) was done under nitrogen using a Perkin Elmer Pyris 1 TGA instrument operating from 100 to 700 °C at a heating rate of 10 °C/min. Fourier transform infrared (FTIR) spectra were acquired using a Nicolet 360 FTIR spectrophotometer with a single bounce attenuated total reflectance (ATR) accessory (diamond crystal). Atomic force microscopy (AFM) images were obtained using a Bruker Multimode 8 atomic force microscope with NanoScope V controller in the PeakForce Tapping[™] mode under ambient conditions. The polymer samples were clamped into a cross-section holder and cut into a triangle using a razor blade. The triangle was trimmed using a Leica UC7 with a Diatome Ultra diamond knife to generate the cross-section for imaging. Each height image was acquired using ScanAssyst[®] to

optimize the variables for the PeakForce Tapping[™] mode of operation. Off-line image analysis was completed using NanoScope Analysis 1.20. Transmission electron microscopy (TEM) images were obtained using a JEOL 1200 EX transmission electron microscope. The samples were sectioned using a Leica UC7 ultramicrotome with Diatome Ultra diamond knife and placed onto a c-flat holey carbon grid.

2.4.3. Water contact angle measurements

Static water contact angles of PBI, 6FDD, and ZIF-8 films were measured using a goniometer with the aid of the software (Drop Shape Analyzer, Model DSA30, KRÜSS GmbH – USA, Matthews, NC). Deionized water, 5 μL , was applied on the sample surfaces using a micro syringe and all the measurements were analyzed by the software. Thin films of polymers were prepared by spin coating 5 mg mL⁻¹ solutions of polymers in DMAc on silicon wafers. A ZIF-8 film was also prepared following the same procedure using a 5 mg mL⁻¹ colloidal ZIF-8 dispersion. All the films were annealed under vacuum at 100 °C overnight prior to the measurements. Two films of each material were prepared and 5 water contact angle measurements from each film were obtained and the averages are reported.

3. Results and discussion

3.1. Synthesis of the 6FDD

Characterization of the synthesized 6FDD is provided in the [supplementary information](#).

Completion of the 6FDD (3:2) imidization was confirmed by the ATR-FTIR spectroscopy (Figure S1). TGA results show that the polymer is thermally stable up to 450 °C (Figure S2). The GPC

results indicate that the polymer has a weight average molecular weight (M_w) of 170,000 with a PDI of 2.3. The polymer structure was confirmed by ^1H NMR spectroscopy (Figure S3).

3.2. Membrane characterization

3.2.1. Microstructure of the blend membrane

The membrane microstructure was confirmed by SEM, AFM and TEM imaging.

The morphology of the 6FDD:PBI (50:50) membrane was investigated with SEM imaging on freeze-fractured cross-sections (Fig. 3A). To confirm the identities of the dispersed and continuous phases, samples of the membranes were subjected to Soxhlet extraction using THF, which selectively removed 6FDD. Fig. 3B shows an SEM image of a 6FDD:PBI (50:50) THF-extracted membrane confirming that the dispersed phase is 6FDD and the continuous phase is PBI. When 5% (w/w) ZIF-8 was incorporated into the 6FDD:PBI (50:50) blend, the domain sizes of the 6FDD became smaller and more uniform compared to the pure polymer blend (Fig. 3C). This effect can be further illustrated by the histograms in Fig. 4. For the 6FDD:PBI (50:50) blend (Fig. 4A) the average domain size of the dispersed phase is large and shows a wide distribution ($1.46 \pm 0.60 \mu\text{m}$). However, when only 5% (w/w) ZIF-8 was added to the same blend (Fig. 4B), the average domain size decreased to $0.33 \pm 0.07 \mu\text{m}$. Not only did the dispersed domains become smaller, but they also became more uniform in size upon the incorporation of ZIF-8.

AFM and TEM images (Fig. 5) were also acquired for both membranes and compared with SEM images. Similar to the SEM images, the AFM and TEM images show that the domain size of the dispersed phase becomes smaller and more uniform upon the addition of ZIF-8.

As the ZIF-8 loading was increased to 10% (w/w), the domain size of the 6FDD phase became even smaller in size (Fig. 6A, B). The average diameter of the dispersed phase decreased to $201 \pm 0.03 \text{ nm}$, which is a 100 nm reduction compared to that of the 5% (w/w) ZIF-8 MMM (Fig. 6C, D).

3.2.2. Compatibilization shown by ZIF-8

A more uniform dispersion of one polymer phase in another indicates a better compatibility between the two polymer materials [35,36]. As seen in Figs. 3–6 it is clear that the 6FDD domain sizes in the MMMs have been reduced significantly and have become more uniform in size upon the addition of ZIF-8 as compared to those of the pure polymer blend. This result shows that the compatibilizing efficiency of ZIF-8 in 6FDD:PBI blends is significant even at low ZIF-8 concentrations. A similar observation was reported by Wu and coworkers in compatibilizing a polyamide–polyphenylene oxide immiscible polymer blend using graphene oxide sheets [35]. They

also observed that when the graphene oxide concentration was increased, the size of the dispersed phase domains became even smaller.

The compatibilization observed here can be attributed to both thermodynamic and kinetic factors. In the fabrication of the pure polymer blend membranes, when the two polymer solutions were mixed together, the solution remained clear, suggesting that the two polymer phases were well-mixed in the presence of excess solvent. However, as the solvent evaporated, the solution became turbid due to phase separation. Normally, in a phase-separated polymer blend, phase coarsening takes place with time as a result of coalescence lowering the interfacial tension [2]. In the pure polymer blend membrane this process results in a non-uniform distribution of the domain sizes of the dispersed phase. In the MMMs, with the ZIF-8 nanoparticles being dispersed first in PBI prior to the addition of 6FDD, the phase separation of the two polymers still takes place upon solvent evaporation, but under a restriction for coalescence of the dispersed 6FDD domains.

This phenomenon is well known in emulsion chemistry, where certain additives can compatibilize immiscible polymers by inhibiting coalescence [37,38]. Likewise, nano fillers have also been shown to compatibilize immiscible polymer blends due to the restriction of coalescence [39–41]. Furthermore, as the ZIF-8 loading increases, the domain size becomes even smaller due to greater restriction for coalescence.

To our knowledge, this is the first report using MOF/ZIF nanoparticles to control the nanostructure of an immiscible polymer blend.

The next important factor to consider is the location of the ZIF-8 nanoparticle. (Attempts made to locate the nanoparticle in the polymer matrix with energy dispersive X-ray spectroscopy were unsuccessful due to the small amount of nanoparticles used.) However, the location of ZIF-8 nanoparticles can be predicted using SEM, AFM and TEM microscopy data in conjunction with a theoretical model. Equation (1) must be satisfied for a nanoparticle (NP) to be driven to the interface of two immiscible polymers, under thermodynamic control [42]. Otherwise, the NP could aggregate in either of the phases depending on the interfacial tension (Equation (2)).

$$|\sigma_{\alpha}/\text{NP} - \sigma_{\beta}/\text{NP}| < \sigma_{\alpha}/\beta \quad (1)$$

$$\sigma_{\alpha}/\text{NP} < \sigma_{\beta}/\text{NP} \quad (\sigma_{\alpha}/\text{NP} > \sigma_{\beta}/\text{NP}) \quad (2)$$

where σ is the interfacial tension; α and β are the different phases.

σ_{α} values cannot be measured experimentally, but can be derived from surface tension values (γ) calculated using water contact angles (WCA) [42,43]. Following this approach, water

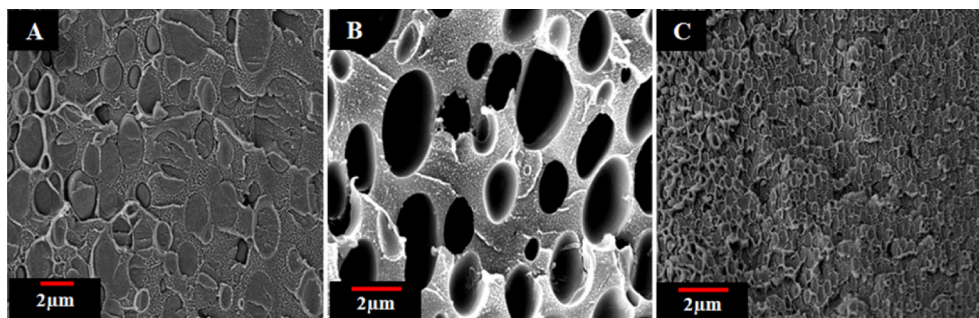


Fig. 3. SEM images of 6FDD:PBI (50:50) membrane cross-section (A) before and (B) after selective THF extraction of 6FDD, and (C) 5% (w/w) ZIF-8 6FDD:PBI (50:50) membrane.

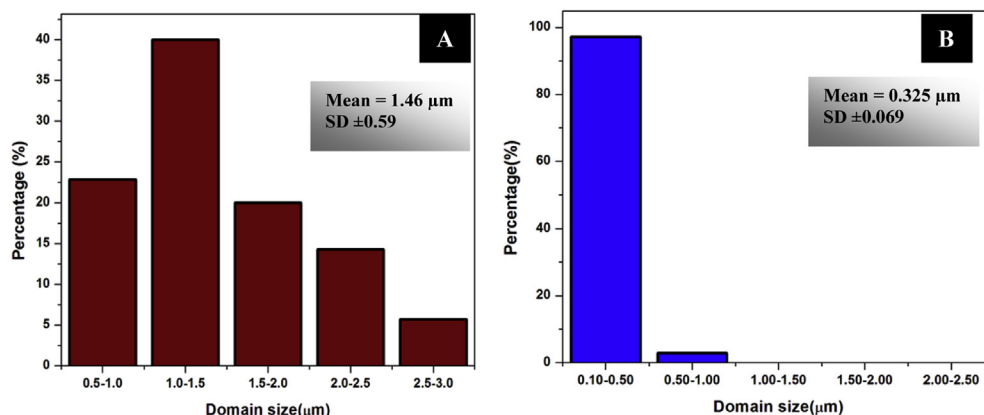


Fig. 4. Histograms of the domain sizes of the dispersed phase in (A) 6FDD:PBI (50:50) and (B) 5% (w/w) ZIF-8 6FDD:PBI (50:50) membranes.

contact angles for ZIF-8, 6FDD, and PBI were measured using a goniometer (Figures S4–S6). The measured WCAs are comparable with the values reported in literature [44–46]. 6FDD has $-\text{CF}_3$ groups belongs to the 6FDA monomer (Fig. 1) and accounts for the high hydrophobicity indicated by a higher WCA. Recently, Guangming et al. reported the WCA values of 6FDA based polyimides and reported an increase of water contact angle as the $-\text{CF}_3$ content increases [44]. The WCA measured for PBI is also comparable with the reported values [45] and the WCA measurements obtained for ZIF-8 were slightly less than that of ZIF-71 reported recently by Dong and Lin [46]. After obtaining the WCAs, by substituting in Equation (3) (Table 1), γ values of ZIF-8, 6FDD, and PBI were calculated (Table 2).

$$\gamma_s = \gamma_l(1 + \cos \theta)^2/4 \quad (3)$$

where γ is the surface tension, s is the solid, l is the liquid, and θ is the water contact angle ($\gamma_l = 72 \text{ mN m}^{-1}$ [47])

Then, the interfacial tension values (σ) (Table 2) of the three components, 6FDD, PBI, and ZIF-8, were calculated from their surface tensions using the Girifalco-Good equation (Equation (4)) [41]

$$\sigma_{1,2} = \gamma_1 + \gamma_2 - 2(\gamma_1\gamma_2)^{1/2} \quad (4)$$

where $\sigma_{1,2}$ ($\sigma_{\alpha/\text{NP}}$, $\sigma_{\beta/\text{NP}}$, or $\sigma_{\alpha/\beta}$ in Equation (1)) is the interfacial tension between components 1 and 2

$\sigma_{6\text{FDD}/\text{PBI}}$ is the highest between the three interfaces considered. This could be due to the high interfacial tension built due to the immiscibility between the polymers. The $\sigma_{\text{ZIF-8}/\text{PBI}}$ and $\sigma_{\text{ZIF-8}/6\text{FDD}}$ values are lower than that, suggesting a better compatibility between ZIF-8 and both polymers. The $\sigma_{\text{ZIF-8}/\text{PBI}}$ value is slightly lower than that of $\sigma_{\text{ZIF-8}/6\text{FDD}}$ which could be attributed to the presence of similar imidazole functionalities resulting in somewhat uniform surface chemistry. Furthermore, in the literature it has been reported that loadings of ZIF-8 as high as $\sim 58.7 \text{ wt.}\%$ have been

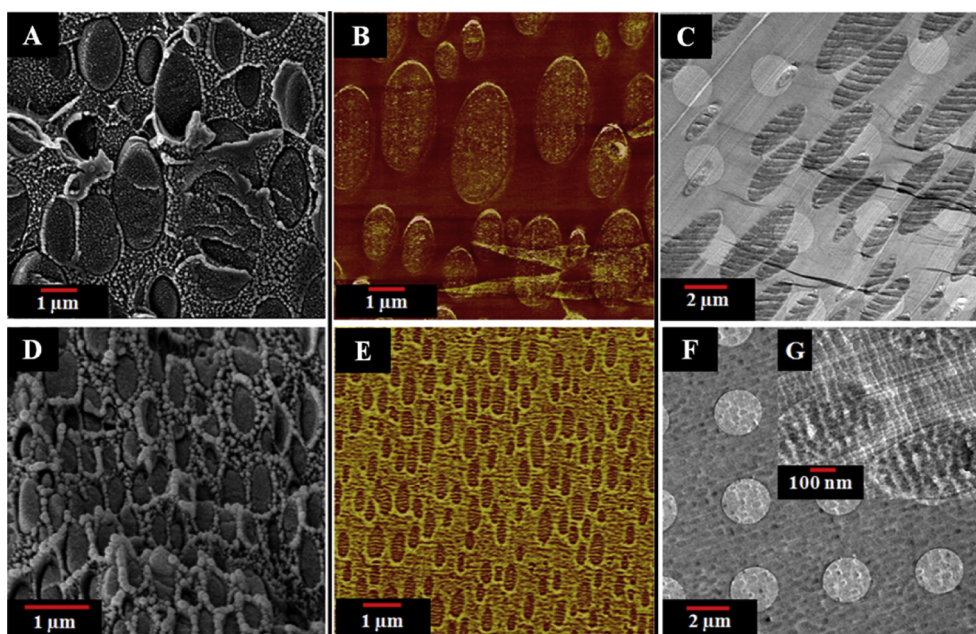


Fig. 5. (A) SEM, (B) AFM, (C) TEM images of 6FDD:PBI (50:50) blend membrane cross-sections and (D) SEM, (E) AFM, (F,G) TEM images of 5% (w/w) ZIF-8 6FDD:PBI (50:50) membrane cross-sections.

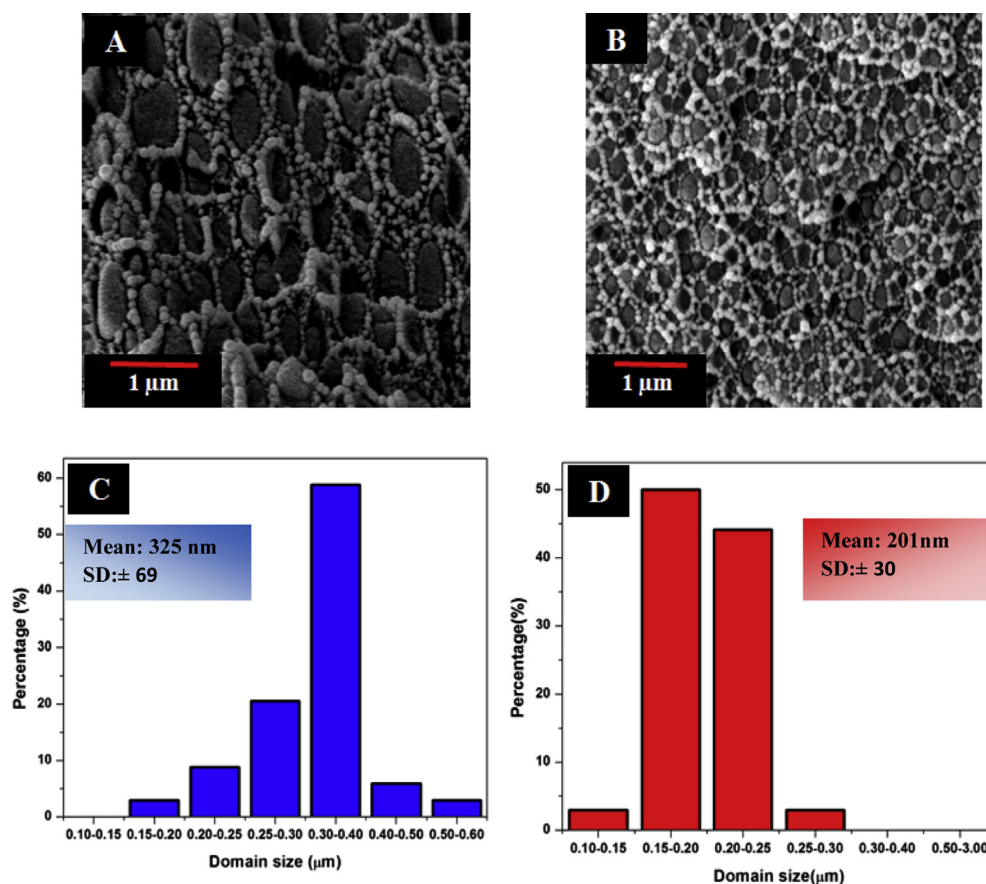


Fig. 6. SEM images of 6FDD:PBI (50:50) with (A) 5% (w/w) ZIF-8 and (B) 10% (w/w) ZIF-8, and histograms of 6FDD:PBI (50:50) with (C) 5% (w/w) ZIF-8 and (D) 10% (w/w) ZIF-8.

incorporated into PBI due to the compatibility between ZIF-8 and PBI [48]. Since $\sigma_{\text{ZIF-8/PBI}}$ is slightly lower than $\sigma_{\text{ZIF-8/6FDD}}$, one might expect that ZIF-8 would preferentially mix with PBI. However, $\sigma_{\text{PBI/6FDD}}$ is actually higher than the difference between the individual nanoparticle/polymer interfacial values, satisfying the condition of Equation (1) that is required to drive the nanoparticle to the interface under thermodynamic control.

Furthermore, substituting the σ values (Table 2) into Young's equation (Equation (5)) predicts a ZIF-8 contact angle in 6FDD of 85.4° (Fig. 7), which is consistent with the morphology observed.

$$\sigma_{\text{ZIF-8/PBI}} + \sigma_{\text{PBI/6FDD}}(\cos \theta) = \sigma_{\text{ZIF-8/6FDD}} \quad (\theta = 85.4) \quad (5)$$

Since the NPs were equally wetted by the polymers, the contact angle would be 90° and the NP is localized at the interface under thermodynamic control. This computational prediction is consistent with our experimental observation that the uniform and smaller domain sizes of the polymer phases in the MMMs are achieved with the addition of ZIF-8 NPs.

Another possible distribution of the NPs is their random location throughout either of the polymer phases. If ZIF-8 localized in the 6FDD phase, then the smaller and uniform domain sizes of the

6FDD phase would not be expected because the domain size of the dispersed phase would become larger due to the lack of restriction for coalescence. A random distribution of NP would result in a wide range of domain sizes as observed for pure polymer blend membranes. This is not observed and the ZIF-8 NPs are predicted to localize at the interface thus lowering the interfacial energy and yielding finer and uniform domain structures.

4. Conclusion

In summary, two immiscible high performance polymers (6FDD and PBI) were compatibilized with ZIF-8 NPs. This was confirmed by analysis of the membrane microstructures using SEM, AFM and TEM imaging. An MMM containing 5% (w/w) ZIF-8 exhibited small and uniform domain sizes of the high permeability dispersed phase (6FDD) in the highly selective continuous phase (PBI). The microstructure is in contrast to the nonuniform domain distributions in membranes of the polymer blend without additives. As the ZIF-8 loading was further increased to 10% (w/w), the 6FDD domain size became even smaller, suggesting even higher compatibility of the polymers. This effect was attributed to the overall lowering of the interfacial energy due to localization of ZIF-8 at the interface of

Table 1
Calculated surface tension values (γ) using water contact angles.

Film	θ ($^\circ$)	γ (mN m $^{-1}$)
PBI	73.3 ± 3.3	29.81
6FDD	101.5 ± 3.2	11.54
ZIF-8	86.4 ± 3.7	20.34

Table 2
Calculated interfacial tension (σ) values.

Interface	σ (mN m $^{-1}$)
PBI/6FDD	4.26
ZIF-8/6FDD	1.24
ZIF-8/PBI	0.90

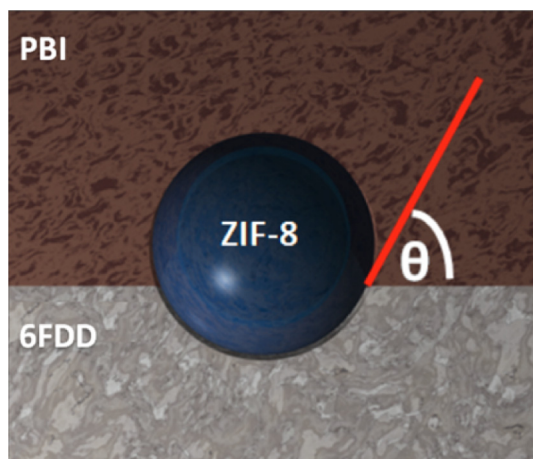


Fig. 7. Localization of ZIF-8 at the interface of 6FDA-DAM:DABA and PBI.

the two immiscible polymers as verified by both microscopy and a theoretical calculation based on water contact angle measurements. These MOF-compatible blends may open up opportunities for blends of otherwise incompatible polymers in a variety of applications including membrane-based separations.

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Appendix A. Supplementary material

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.03.008>.

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