

Synthesis and Physicochemical Characterisation of Amine Functionalised SiO₂/PBI derivatives nanocomposite membrane

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ABSTRACT

In this study, a series of amine functionalised silica/OPBI nanocomposite membrane for high-temperature polymer electrolyte fuel cell (HT – PEMFC) application were prepared. In order to provide a better dispersion and improving the interfacial interaction between organic/inorganic materials, polyethyleneimine was immobilised onto the surface of silica before added into poly(4,4'-diphenylether – 5, 5'-bibenzimidazole) (OPBI). Nuclear Magnetic Resonance (NMR) experiment proved the synthesised polymer while Fourier-transform infrared spectroscopy (FTIR) and EDX method used to validate the grafting of the amine derivative to the surface of silica in the polymer matrix. Although a satisfactory dispersion pattern was found on all nanocomposite membrane under scanning electron microscope (SEM) studies, agglomeration pattern was seen at higher loading of functionalised silica nanoparticles. The physicochemical characteristic of the nanocomposite membrane was investigated by using thermogravimetric analysis for high temperature PEMFC application. Lower water uptake and swelling ratio in both water and phosphoric acid (PA) showed by the OPBI / SiPEI with an increasing trend as the amount of SiPEI were increased. Addition of amine functionalised silica into OPBI shows a significant improvement compared to pure OPBI while the thermal stability of the membrane at high temperature region (100 – 200 °C) can be influenced by the loading concentration of the amine functionalised silica.

Keywords: Polybenzimidazole; Nanocomposite; Proton exchange membrane; Surface functionalisation

INTRODUCTION

PEMFC faced several issues such as slow kinetic reaction, CO tolerance and have bad a heat and water management when operated at lower side (< 80 °C) (Bashuk et al. 2001; Li et al. 2003 & Asensio et al. 2010). Operating PEMFC at a higher temperature (100 – 200 °C) are one of the ways to overcome the problems. Commercial ready membrane which are commonly used for PEMFC such as Nafion; unable to operate at high temperature due to membrane degradation and loss of proton conductivity when operated at a temperature more than 80 °C. Alternative candidate such as phosphoric acid doped polybenzimidazole (PBI) are selected as membrane for HT-PEMFC as it displays good thermal stability and able to operate at temperature up to 200 °C without humidification (Qingfeng et al. 2007).

To solve the issue in phosphoric acid doped PBI membrane such as low mechanical properties caused by high doping level and acid leaching from the membrane in extreme temperature, research has tried to tackle the issue with different approaches and incorporation of inorganic particle are one of available way that piques researcher interest. Until now, most studies had incorporated PBI with organic filler to provide not only a better proton conductivity but also mechanical and thermal stability (Subianto 2014).

Despite the practise of addition of inorganic filler such as SiO₂ able to improve the mechanical stability of the PBI membrane, the proton conductivity of the nanocomposite will be compromised (Pu et al. 2009). In addition, SiO₂ tends to agglomerate easily especially at high concentration during the mixing with the polymer matrix limits on how thin the nanocomposite membrane can be. Since a good dispersion of nanometre-sized particles has significant impact on the properties of the nanocomposite, a method to produce a good dispersion and homogenous mixture between polymer and silica nanoparticles need to be carefully selected. On the other hand, SiO₂ being in favour among researchers due to its versatility when it comes to surface modification. Chemical modification such as silane coupling agent can be used to enhance the dispersion quality and its interfacial interaction.

In previous studies, a short and long- chained amine-modified onto the surface of silica has been demonstrated by using 3-aminopropyltriethoxysilane (APTES) (Ghost et al. 2011) which having a primary amine group and *N*-(3-trimethoxysilylpropyl) diethylenetriamine (TMSPTD) (Singha et al. 2014) which having three amine functional groups respectively before being incorporated into poly(4,4'-diphenylether-5,5'-bibenzimidazole) (OPBI) polymer (Figure 1); a derivatives of PBI. Specific crystalline pattern was found in both amine functionalised silica compared

to unmodified nanoparticles. A robust structure of silica nanoparticles was observed at three-amine functionalised silica nanocomposite. In addition, the research also claimed that the proton conductivity of the amine-modified silica nanocomposite is better due to the presence of abundance -NH_2 moiety in the three-amine functionalised group modified silica as it provides more proton hopping site compared to a primary amine group modified silica which contributes to the increase of proton conductivity of the membrane.

By referring to the previous work, the potential of nanocomposite OPBI with a longer/complex amine functionalised silica as a modifier was synthesised in order to understand better performance of amine functionalised silica nanocomposite. Trimethoxysilylpropyl-polyethyleneimine (TMS-PEI) which having a complex structure of -NH_2 group were immobilised onto the surface of silica to allow a better membrane property that might occur due to longer chain and stronger multiple point interaction between the abundance of -NH_2 in polyethyleneimine on the filler surface and the polymer matrix.

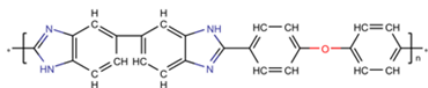


FIGURE 1. Chemical structure of OPBI polymer

MATERIALS AND METHODS

MATERIALS

4, 4'-oxybis (benzoic acid) (OBA) was purchased from Alfa Aesar. 3, 3', 4, 4'- tetraaminobiphenyl (TAB, polymer grade) was obtained by Sigma Aldrich. Trimethoxysilylpropyl polyethyleneimine (TMS-PEI, 50% in *i*PrOH) was supplied from BOC Science, USA. Silica nanoparticles (average particles size 20 - 30 nm) was obtained from SAT nano Technology Material Co. Ltd, China. Polyphosphoric acid (PPA, 115%), Formic acid (FA, 99%), Toluene and Ethanol were purchased from Fisher Scientific (M) Sdn Bhd. All mentioned chemical was used without further purification.

SYNTHESIS OF OPBI

OBA (1.82 g) and TAB (2.19 g) were added into a three-necked, round bottom flask together with polyphosphoric acid (PPA) (100 g). The reaction system was equipped with a mechanical overhead stirrer and also purged with nitrogen gas which was maintained throughout the process. The polymerisation reaction temperature was controlled between 190 – 200 °C and lasted for approximately 26 hr. At the end of the polymerisation, a dark brown colour with vicious mixture can be seen. The mixture is then poured into double distilled water and separated as brown mass. The obtained mass is then collected, neutralised with sodium carbonate, washed thoroughly with water and dried in a vacuum oven

for 24 hours at 100 °C to dry for further characterisation (Sannigrahi 2009).

SILICA SURFACE MODIFICATION

A desired amount of silica nanoparticles was dispersed in 200 mL dry toluene and bubbled with N_2 for 30 mins. Trimethoxysilylpropyl-polyethyleneimine (TMS-PEI) were added dropwise to the dispersion and the mixture was left to stir at room temperature before the temperature of the environment was increased to 110 °C. It was then refluxed for 24 hours under dry nitrogen. The suspension mixture of TMS-PEI/ SiO_2 is then let cooled before it was centrifuged and then washed with methanol and water and then centrifuged again to separate the solid from the solvent mixture. The solid was collected and then transferred to dry in a vacuum oven at 60 °C for 12 h (Czaun 2013). The functionalised silica is being called as SiPEI from this point forward.

FABRICATION OF OPBI/SIPEI NANOCOMPOSITE MEMBRANE

To prepare amine functionalised silica/OPBI nanocomposite membrane, 3, 5, 7, and 10 wt. % (with respect to polymer concentration) nanoparticles was dispersed in formic acid and added into a 2 wt. % polymer solution in formic acid. The final concentration in solution was 1 wt. %. The mixture solution was left to stir at room temperature for 24 hours to form homogenous mixture before poured on glass Petri dish to let the solvent to evaporate. The membrane is then peeled off the Petri dish and left to dry in an oven at 100 °C to remove any trace solvent molecules before stored in a zip-lock airtight bag for further analysis. The functionalised OPBI/ SiO_2 are also prepared with the loading of 5 and 10 wt. % with the same procedure mentioned above for comparison purpose.

CHARACTERISATION METHOD

^1H NMR spectra are recorded with a Bruker Ultra Shield Plus 500-MHz NMR spectrometer at room temperature with $\text{DMSO}-d_6$ used as solvent. The inspection of a single component in the nanocomposite was conducted using Nova Nanosem 230 (FEI, Netherlands). An EDX spectroscopy are attached to ultra-high-resolution field emission scanning electron microscope (FESEM). Fourier transform infrared (FT-IR) spectra of synthesised membranes and powder samples were recorded in the attenuated total reflectance (ATR) mode in the frequency range of 4000 - 400 cm^{-1} on a Nicolet iS10 instrument equipped with Smart iTX sampling accessory (Thermo Scientific, USA). The spectrum was recorded as the average of 9 scans with a resolution of 16 cm^{-1} . Inspection of the cryo-fractured surfaces of synthesised nanocomposite membrane was conducted by scanning electron microscopy (SEM) using a Hitachi VP-SEM SU1510. Films were covered with conductive gold coating, by using a Hitachi E1010 Ion Sputter before running through the SEM.

Thermogravimetric/differential thermal analysis (TG-DTA) was carried out on a Mettler Toledo TG-DTA instrument from 30 – 800 °C at a scanning rate of 10 °C /min in the presence of a nitrogen flow of 50 ml/min. Oxidative stability were tested by immersing the membrane in the Fenton's Reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 70 °C and the time when the membrane starts to break into pieces were measured. For water uptake and swelling ratio measurements in both water and acid, the membranes were dried thoroughly in a vacuum oven at 100 °C for 3 days. Equally sized of membranes were prepared and their weights were measured. They were then immersed in distilled water for 3 days (for measurements in water) and in PA (for measurements in acid) for 7 days. After the specified time frame, the wet membranes were mopped with filter paper and their weights are measured again. Water uptake and swelling ratio were calculated as:

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

$$\text{Swelling ratio in water \& PA} = \frac{L_w - L_d}{L_d} \times 100\% \quad (2)$$

RESULT AND DISCUSSION

NMR AND EDX ANALYSIS

Figure 2 shows the representative of ¹H NMR spectra of synthesized OPBI in DMSO-d₆ together with peak assignment and chemical structure. As per expected chemical structure, the peaks assigned in the spectra shown are in good agreement as in past literature. A doublet peak at 7.32 ppm is assigned to H_a while at 7.57 ppm are assigned to H_b as can be seen in Figure 1. A peak of doublet seen at 7.67 ppm are assigned to H_c and a singlet peak are assigned to H_d. A doublet at 8.29 ppm is assigned to H_e (Kojima 1980). From the EDX method (Figure 3), the atom in the sample are identified at the depth between 10 – 1000 nm of the surface of the sample revealed the distribution of C, O, and Si atoms. From the sample taken, the presence of Si atom can be seen although the Si peak is quite low indicated that most cases polymer on the surface of the silica existed.

FTIR ANALYSIS

OPBI films with approximately 25 μm thickness were examined with FTIR spectrometer for FTIR measurements. The vibration at 1050 cm⁻¹ are assigned to the Si – O – Si antisymmetric frequency of functionalised silica nanoparticles which is visible in all nanocomposite membrane spectra as in Figure 4. The band around 1445 cm⁻¹ refers to the in-plane deformation of benzimidazole rings (Robert et al. 2005). A visible peak at 1160 cm⁻¹ which has been assigned to the ether linkage of OPBI (Lobato et

al. 2006). The characteristic peaks at 3320, 3156 and 3064 cm⁻¹ in Figure 5 are assigned to the stretching frequency of the free – NH groups, the broad transmission due to the stretching bonded – NH groups and a low intense peak due to the frequency of aromatic groups respectively.

A declined in the intensity of peaks of N – H functionality in the nanocomposite membrane as the number of nanoparticles used in the composite membrane increased suggesting that the formation of hydrogen bonds between amine group of polymer and functional groups of functionalised silica nanoparticles (Singha et al. 2014). The presence of a weak band at 3369 and 3302 cm⁻¹ in Figure 6 which attributed to N – H stretches (Socrates 2004) shows that SiPEI has been successfully functionalised. Symmetric and asymmetric stretching band of – CH₂ which can be seen at and 2950 and 2835 cm⁻¹ comes from chain. In addition, absorption band around 1560 and 1465 cm⁻¹ are attributed to asymmetric and symmetric bending of primary amine (– NH₂) (Socrates 2004) and absorption band at 1650 cm⁻¹ are assigned to the bending of secondary amines group (– N(R) H of chain (Stuart 2004) which can be seen in Figure 6.

SEM ANALYSIS

The dispersion of polyethyleneimine functionalised silica nanoparticles in the OPBI matrix were analysed by examining the surface and the cross-section of OPBI/SiPEI with different loading using SEM image. Referring to Figure 7, a satisfactory dispersion pattern on the surface of the membrane were found at all nanocomposite membrane. On the other hand, agglomeration of the nanoparticles were seen in Figure 7(a – b) as the loading of polyethyleneimine functionalised silica nanoparticles increased especially at 7 and 10 wt. % were used. No separation phase between organic/inorganic material can be seen for all nanocomposite membrane as portrayed in Figure 8. It can be said that functionalised silica nanoparticles dispersed uniformly all over the OPBI matrix.

THERMAL ANALYSIS

Thermal stability of pure OPBI along with the fabricated nanocomposite membrane was found in Figure 9, 10 and 11. Thermogravimetric analysis was performed at a heating rate of 10 °C /min under a flow of nitrogen atmosphere. Initial weight loss can be seen in Figure 9 around 130 °C which comes from loss of water molecules. Second weight loss occurred at 230 °C (Figure 10) primarily caused by the degradation of the polymer chain. When the temperature continues to arise, all fabricated OPBI/SiPEI nanocomposite experienced decomposition of complex amine chain molecules which presents on the silica surface which then contributed to the degradation of the polymer chain. In the case of OPBI/SiPEI 10 wt. %, apart from pure OPBI it experienced the highest weight loss compared to others. These behaviours probably caused by the decomposition of complex amine chain at higher temperature contributed by agglomeration of nanoparticles. However, since our

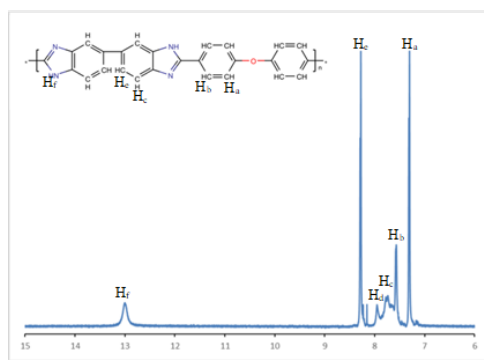


FIGURE 2. ¹H-NMR spectrum of OPBI in DMSO – d₆

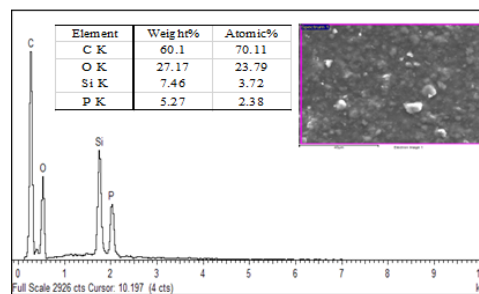


FIGURE 3. EDX data for OPBI/SiPEI

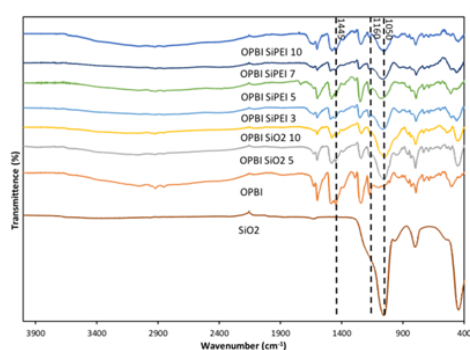


FIGURE 4. IR Spectra of OPBI, SiO₂ and OPBI/SiPEI nanocomposite with their indication loadings

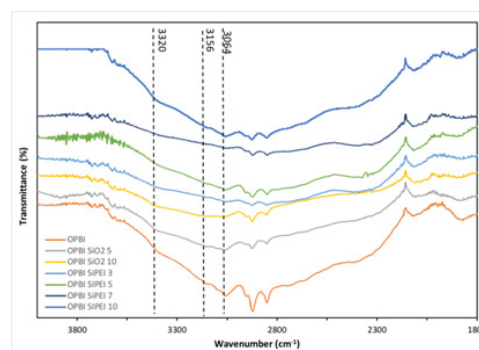


FIGURE 5. IR Spectra of OPBI and OPBI/SiPEI nanocomposite membrane with their indicated SiPEI loadings

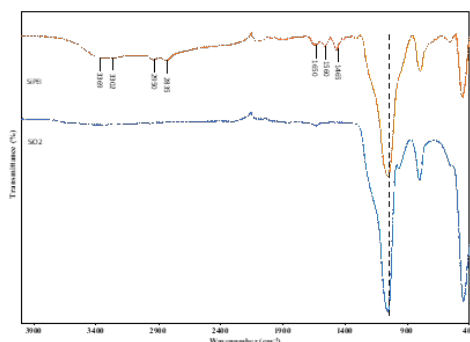


FIGURE 6. IR Spectra of SiO₂ and SiPEI

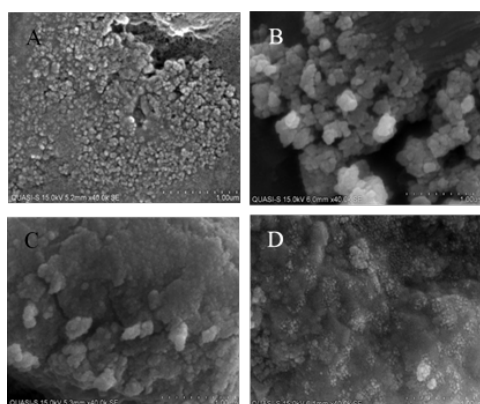


FIGURE 7. SEM images of the surface on the nanocomposite membrane a) OPBI/SiPEI 3% b) OPBI/ SiPEI 5% c) OPBI/ SiPEI 7% and d) OPBI/ SiPEI 10%.

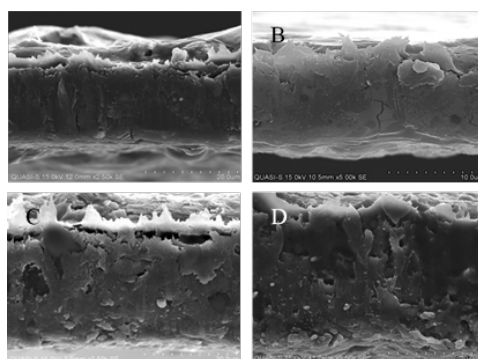


FIGURE 8. SEM images of the cross section of the nanocomposite membrane a) OPBI/SiPEI 3% b) OPBI/SiPEI 5% c) OPBI/SiPEI 7% and d) OPBI/SiPEI 10%

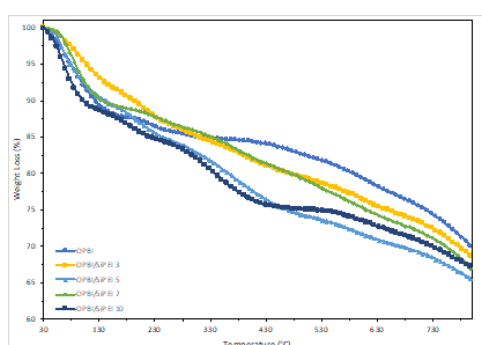


FIGURE 9. TGA plots of OPBI and its nanocomposite membranes with various percentages of SiPEI loadings

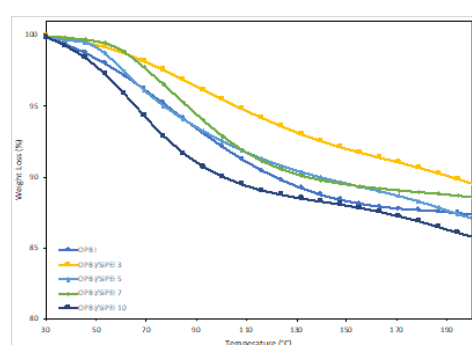


FIGURE 10. TGA plots of OPBI and its nanocomposite membranes with various percentages of SiPEI loadings between 30 - 300 °C

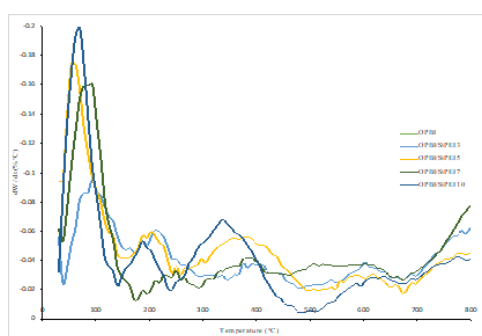


FIGURE 11. DTG plot of OPBI and its nanocomposite membrane

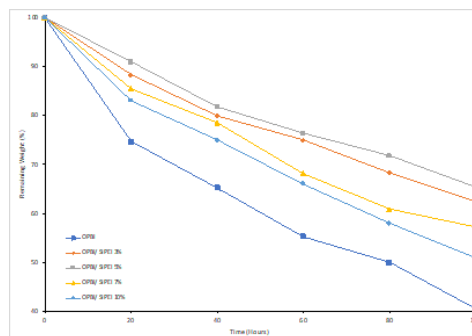


FIGURE 12. Oxidative stability of OPBI nanocomposites with different loadings of SiPEI

particular interest focused on the region 100 – 200 °C as operating temperature of HT – PEMFC, it could be said that all nanocomposite membrane shows an increase of thermal stability compared to pure OPBI.

As it is observed in the region between 100 – 200 °C, addition of 3 to 7 wt. % of SiPEI helps in improving the thermal stability of the nanocomposite membrane compared to pure OPBI while its performance worsens as the loading of SiPEI were increased to 10 wt. %. While at 200 °C, almost all OPBI/SiPEI nanocomposite experienced weight loss compared to OPBI. The lowest weight loss showed by OPBI/SiPEI 3 wt. % and the highest weight loss showed by OPBI/

SiPEI 10 wt. % which experienced 10% and 15% weight loss respectively. This suggesting that addition of SiPEI into OPBI matrix do help in improving the thermal stability. However, excessive amount of SiPEI may contribute to heavily complex structure which results in deterioration of the thermal properties of the nanocomposite membrane at the higher temperature.

OXIDATIVE STABILITY

The oxidative stability of the nanocomposite membrane as a function of time is illustrated in Figure 12. All

the nanocomposite membrane shows higher chemical stability compared to pure OPBI. All the nanocomposite membrane shows higher chemical stability compared to pure OPBI. However, as the increased in the loading of SiPEI, the stability of stability increased before the stability deteriorates as the loading of SiPEI increased to 7% and above. This suggesting that addition of complex amino chain contributes to protecting the polymer from radical attack by performing network all over the matrix. Theses protection may be attributed to hydrogen bonding interaction between TMS – PEI on the silica surface and OPBI chain although at the higher loading the performance starts to deteriorate. Hence, as loading increases at certain concentration; there is more ionic interaction and able to provide protection to polymer chain which contributes to improving the durability in an oxidative stability environment, making these nanocomposite membranes suitable for PEM application.

WATER UPTAKE AND SWELLING RATIO IN WATER AND PA

The water uptake and swelling ratio in both water and PA of OPBI nanocomposite membranes obtained with SiPEI were tabulated in Table 1. After the immersion of the membrane in distilled water for 3 days; it was found out pure OPBI absorbed approximately 20.68% of water compared to its dry state. The water uptake and swelling ratio of all OPBI/SiPEI nanocomposite membrane are lower compared to pure OPBI. Although, it needs to point out that an increasing trend was observed as the amount of SiPEI used increased. Similar to TGA data (Figure 9), an increase of initial weight loss are seen as the loading of SiPEI were increased. OPBI are hydrophilic in nature, hence the agglomeration of silica formed (Figure 7) when the amount of SiPEI loading was increased suggesting that more water molecule was getting bonded with –N= atom of OPBI rather than –N= atom of OPBI to form hydrogen bond with PEI chain on the silica surface. This probably caused more water uptake and more initial weight loss are seen in the TGA data as the loading of SiPEI in the nanocomposite membrane were increased.

In previous studies that using OPBI as a derivate of PBI membrane, the thermal stability of OPBI are quite excellent. Under temperature below 200 °C, the weight loss around 5 wt. % was recorded (Dai et al. 2010 and Li et al. 2012). Although OPBI/SiPEI displayed slightly higher weight loss (around 10 wt. % under 200 °C), there are also similar studies which are recorded by Ghosh et al. 2011, Ni et al. 2016 and Devrim et al. 2016.

On the other hand, as for the oxidative stability; OPBI/SiPEI behaved slightly lower compared to nanocomposite prepared by Ghosh et al. 2011 (highest weight remaining around 75%). As for dimensional stability, synthesised OPBI/SiPEI can only prevent the swelling until 6.16% while nanocomposite PBI with pre-oxidized acrylic fiber (POAF) and ferric sulfophenyl phosphate (FeSPP) can prevent swelling up until less than 2% (Sun et al. 2017). Nevertheless, there are studies that show the swelling ratio is higher than 6% (Li et al. 2004 and Namazi 2011) making that synthesised OPBI/SiPEI are not that inferior and have the potential to be used as polymer exchange membrane for HT – PEMFC.

CONCLUSION

In this work, series of nanocomposite membranes of OPBI with polyethyleneimine functionalised silica (SiPEI) was fabricated and the physicochemical where characterised. NMR experiment proved the synthesised polymer is OPBI while from FTIR results, polyethyleneimine were successfully functionalised onto silica and grafted with the OPBI polymer which is also confirmed by EDX method. SEM images show a satisfactory dispersion of nanoparticles on both surface and cross-section of all fabricated nanocomposite membrane although agglomeration formed at a high load of functionalised nanoparticles. As for oxidative stability and thermal stability, the addition of SiPEI to OPBI polymer shows improvement in thermal stability compared to pure OPBI. However, in the case of thermal stability; the amount of SiPEI loading content can influence the thermal stability of the nanocomposite membrane especially at high temperature. In the water uptake and swelling ratio in both water and PA, incorporation of SiPEI improved the membrane properties of both tests. However, as the loading increases the performance of the nanocomposite membrane deteriorated. As a result, polyethyleneimine functionalised silica SiPEI/OPBI nanocomposite membrane has the potential to be used at the high-temperature PEMFC application.

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TABLE 1. Water Uptake, Swelling ratio of water and PA in the OPBI/SiPEI nanocomposite membrane.

Material	Water Uptake (%)	Swelling Ratio	
		Water (%)	PA (%)
OPBI	20.68	7.35	7.51
OPBI/SiPEI 3%	19.15	6.69	7.24
OPBI/SiPEI 5%	17.05	6.16	6.91
OPBI/SiPEI 7%	19.85	7.17	7.87
OPBI/SiPEI 10%	23.33	9.67	8.14

DECLARATION OF COMPETING INTEREST

None.

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