Fabrication and Characterization of Ni(BDC)(TED)$_{0.5}$/Polysulfone Mixed Matrix Membrane

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ABSTRACT

Mixed Matrix Membranes (MMMs) appear to be very potential materials to enable efficient gas permeation. MMMs consist of inorganic particle filler dispersed in a continuous polymeric matrix homogeneously. Among various type of filler materials, Metal Organic Frameworks (MOFs) have been discovered as the potential fillers to be used in fabrication of MMMs due to their high affinity with the polymer chains and high sorption capacity which is contributed by their high porosity properties. In this study, Ni(BDC)(TED)$_{0.5}$, which is a type of MOFs was synthesized via solvothermal method at 120 °C for 48 hours and subsequently incorporated into polysulfone (Psf) matrix in order to fabricate MMMs. The loading of Ni(BDC)(TED)$_{0.5}$ in the MMMs was varied from 5 wt% to 20 wt% in order to study the effect of fillers on the properties as well as CO$_2$ gas permeation performance of the MMMs. The property of the samples were investigated by using characterization method of X-ray diffractometer (XRD) and field emission scanning electron microscope (FESEM) coupled with energy dispersive X-ray (EDX) spectrometry. The synthesized Ni(BDC)(TED)$_{0.5}$ was well crystallized and possessed an irregular elongated shape. FESEM and XRD results showed that Ni(BDC)(TED)$_{0.5}$ was successfully incorporated into Psf polymer matrix. Lastly, gas permeation test was conducted to determine the CO$_2$ gas permeation. In this study, the CO$_2$/CH$_4$ selectivity increased when the filler loading increased from 5 wt% to 10 wt%, and the optimum CO$_2$/CH$_4$ selectivity of 11.75 was obtained with 10 wt% of Ni(BDC)(TED)$_{0.5}$ incorporated into the MMMs.

Keywords: Mixed matrix membranes, metal organic frameworks, Ni(BDC)(TED)$_{0.5}$, CO$_2$

1.0 INTRODUCTION

One of the fastest growing branches of membrane technology is the development of gas separation membranes [1]. The gas separation is performed via selective transport through polymeric membranes. Membrane technology has been applied widely in various industries. By using the technology of membrane gas separation, targeted components are separated from their mixtures through membranes via pressure gradient or concentration gradient [2]. There are two general types of membranes, namely pure polymeric membranes and inorganic membranes. The gas separation processes using polymer membrane separation

technology offer advantages such as environmentally benign, simplicity and versatility. However, the main constraint in the development of these pure polymeric membranes for gas separation applications is the trade-off between permeability and selectivity where ideally, membranes should exhibit high selectivity and high permeability. On the other hand, inorganic membranes offer good thermal and chemical stability, with high selectivity and gas flux [3]. However, the disadvantage of inorganic membranes is their high fabrication costs. They are also commonly fragile and difficult to be transformed into a high surface area module [1]. In view of the advantages and disadvantages of pure polymeric membranes and inorganic membranes, MMMs start to emerge as an alternative candidate in the membrane technology for gas separation processes. MMMs consist of continuous phase which is the pure organic polymer and dispersed phase which is the inorganic materials [4]. Inorganic particles have unique structure, surface chemistry and mechanical strength. Thus, when they are added to the pure organic polymer matrix, the resulting membrane properties become better than pristine polymer membranes. MOFs is one of the common fillers utilized due to their advantages such as large surface area, controlled porosity and affinity towards desired gases to be separated. The addition of MOFs commonly increases the permeability.

There are several methods widely applied in the fabrication of MMMs, which include dry phase inversion, wet phase inversion and dry wet phase inversion [5]. Among the various methods of membrane fabrication, dry wet phase inversion method is commonly used to prepare pristine Psf membranes as well as the MMMs

because this technique can produce a dense active layer and porous layer which is more suitable to be applied for gas separation [5, 6]. However, the major concern for most of the researches is the incompatibility problem between polymeric matrix and the filler. This problem usually leads to poor adhesion at the solid-polymer interface. Therefore, interface voids exist between polymer and filler results in poor distribution of the filler particles. They tend to clump together in the continuous polymeric matrix and cause agglomeration problem. Specifically, a highly permeable polymer with poor selectivity need to match with a filler with high selectivity in order to reach beyond the Robeson trade-off curve for gas separation process [7].

Apart from the conventional filler materials, MOFs have been discovered to be the potential fillers to be incorporated into MMMs for industrial application due to their high affinity with the polymer chains and high sorption capacity which is contributed by their high porosity properties [8]. $Ni(BDC)(TED)_{0.5}$, which is a type of MOFs, is found to have high potential in effective gas adsorption due to its high adsorption capacities and selectivity. Besides, some of the MOFs showed high stability against humidity [9] and temperature of 673 K [10]. They are less susceptible to water vapours as they remain stable when they are chemically attacked by the water molecules [11]. Due to the different charge and coordination number for different metal units, $Ni(BDC)(TED)_{0.5}$ undergoes slower ligand substitution with water vapour, hence exhibiting good stability under humid conditions [12]. Furthermore, the paddle wheel binuclear metal clusters within $Ni(BDC)(TED)_{0.5}$ possess high microporosity, thermal stability, good sorption property and

good magnetic property which is an advanced functional property [8].

In this paper, we report the synthesis of Ni(BDC)(TED)$_{0.5}$ under 120 °C for 48 hours by using solvothermal technique, and the fabrication of MMMs incorporated with Ni(BDC)(TED)$_{0.5}$. The effect of filler loading on the properties of MMMs were investigated. The MMMs samples were characterized for their morphology and crystallinity by using FESEM and XRD. Besides, gas permeation test was performed on the fabricated MMMs to study CO_2 gas permeation.

2.0 METHODS

2.1 Materials

Nickel (II) chloride hexahydrate (>98%) was purchased from Acros Organics. 1,4-benzenedicarboxylic acid (BDC) and N,N-dimethyl-formamide (DMF, EMSURE®, ACS, ISO, Reag. Ph Eur) were obtained from Merck. Triethylenediamine (TED, ReagentPlus®, ≥99%) and polysulfone pellets were purchased from Sigma Aldrich. Nitric acid and tetrahydrofuran (THF) were obtained from Fisher Scientific.

2.2 Synthesis of Ni(BDC)(TED)$_{0.5}$

Ni(BDC)(TED)$_{0.5}$ was prepared by solvothermal method. 1.07 g of Nickel (II) chloride hexahydrate was mixed with 0.60 g of BDC, 0.33 g of TED, and 150 mL of DMF in a beaker at ambient temperature with stirring rate of 320 rpm. Nitric acid was added to the mixture to dissolve any solid chemicals formed until a clear solution was observed. The resultant solution was then transferred into the stainless-steel Teflon lined vessel and heated in the oven at 120 °C for 48 hours. After

synthesis had been done, the crystals formed was filtered out from the solution by using filter paper and washed 3 times using 10 mL of DMF each. The crystal was then dried at 80 °C overnight in the drying oven and thermally activated at 120 °C for 24 hours under vacuum to remove the guest DMF molecules [13].

2.3 Fabrication of Pristine Polysulfone Polymeric Membranes

Psf pellets was dried at 393 K in drying oven overnight to remove excess moisture. 3.29 of Psf pellets was slowly dissolved in 10 mL of THF solvent at room temperature at 200 rpm. The dope solution was stirred at 130 rpm for 18 hours until a viscous solution was formed. The dope solution was then transferred to an ultrasonic bath and repeatedly sonicated and stirred for 4 hours to remove the trapped micro-bubbles. The dope solution was then allowed to stand overnight until no gas bubbles were observed. The resulting dope solution was poured onto a glass plate and casted to form a thin film by using casting knife with gap of 200 μm. The casted thin film was exposed to the air for 20 seconds. The thin film, together with the glass plate was then immersed into a water bath for 1 day. The membrane film was then removed from the water bath and left to dry at room temperature [14].

2.4 Fabrication of Ni(BDC)(TED)$_{0.5}$/ Polysulfone Mixed Matrix Membrane

Psf pellets was dried at 393 K in drying oven overnight to remove excess moisture. For 5, 10, 15, and 20 wt% of Ni(BDC)(TED)$_{0.5}$/Psf MMMs, a predetermined mass of Ni(BDC)(TED)$_{0.5}$ was slowly added into 10 mL of THF solvent at 100 rpm

until $Ni(BDC)(TED)_{0.5}$ was dispersed homogeneously in the solvent. The resulting mixture was sonicated for 30 minutes. 0.32 g of Psf pellets was dissolved into 10 mL of resulting mixture of THF solvent and $Ni(BDC)(TED)_{0.5}$ at 200 rpm and stirred for 4 hours. Additional 2.97 g of Psf pellets was then slowly dissolved in the resulting mixture at 200 rpm. The dope solution was stirred at 130 rpm for 18 hours until a viscous solution was formed. The dope solution was then transferred to an ultrasonic bath and repeatedly sonicated and stirred for 4 hours to remove the trapped micro-bubbles. The dope solution was then allowed to stand overnight until no gas bubbles were observed. The resulting dope solution was poured onto a glass plate and casted to form a thin film by using casting knife with gap of 200 μm. The casted thin film was exposed to the air for 20 seconds. The thin film, together with the glass plate was then immersed into a water bath for 1 day. The membrane film was then removed from the water bath and left to dry at room temperature [14]. Table 1 shows the membranes fabricated in current study.

Table 1 Membranes fabricated in current study

Membrane Samples Name	$Ni(BDC)(TED)_{0.5}$ loading (wt%)
Pristine Psf membrane	0
5 wt% $Ni(BDC)(TED)_{0.5}$/Psf MMM	5
10 wt% $Ni(BDC)(TED)_{0.5}$/Psf MMM	10
15 wt% $Ni(BDC)(TED)_{0.5}$/Psf MMM	15
20 wt% $Ni(BDC)(TED)_{0.5}$/Psf MMM	20

2.5 Characterization

Field emission scanning electron microscope (VPFESEM, Zeiss Supra55 VP) operated at 5 kV was used to characterize the surface and cross sectional morphology of the fabricated membranes as well as the $Ni(BDC)(TED)_{0.5}$ distribution in the MMMs. The membranes were firstly fractured in liquid nitrogen and coated with gold using a sputter coater in vacuum before placed on a sample holder for analysis. Energy dispersion X-ray (EDX) spectrometry (Oxford Instruments INCA x-act) coupled with FESEM was used to obtain the mapping of the cross section of the membranes. The phase purity, crystallographic structure of $Ni(BDC)(TED)_{0.5}$ and the existence of filler in MMMs were studied using high resolution X-ray diffraction, XRD (X'Pert3 Powder and Empyrean, PANalytical) diffractometer. The XRD patterns were obtained at room temperature by using Cu Kα X-ray radiation ranged from 5° to 40° with an increment of 0.02° and exposure time of 0.1s/step.

2.6 Gas Permeation Test

CO_2 and CH_4 single gas permeations were conducted for all the fabricated membranes in order to measure the gas permeance through the membranes. Prior to the gas permeation test, the membrane was sealed in a stainless steel module and then was placed in a gas permeation test rig. Pure CO_2 or CH_4 gas was fed to the membrane in the gas permeation test rig. The gas permeation test was performed at pressure of 6 bar at room temperature. The permeate gas flow rate was

measured using bubble flowmeter. The gas flowrate was then computed by using Equation (1).

$$Q = V / t \qquad (1)$$

where Q is the volumetric gas flowrate (cm^3/s), V is the volume (cm^3) and t is the time required for a gas bubble to travel across a specific volume (s).

The gas permeance through the membrane was then calculated by using Equation (2).

$$P = Q / (\Delta p \; x \; A) \qquad (2)$$

where P is the gas permeance through the membrane [cm^3(STP)/ cm^2.s.cmHg], Q is the volumetric gas flowrate (cm^3/s), Δp is the pressure difference across the membrane (cmHg), and A is the effective membrane area (cm^2). The data of gas permeance is reported in the unit of GPU where 1 GPU = 10^{-6} cm^3(STP)/cm^2.s.cmHg.

The CO$_2$/CH$_4$ selectivity was determined by calculating the ratio of CO$_2$ gas permeance to CH$_4$ gas permeance.

3.0 RESULTS AND DISCUSSION

3.1 Morphology Analysis

Figure 1 shows the FESEM images of Ni(BDC)(TED)$_{0.5}$. From Figure 1, it can be observed that the Ni(BDC)(TED)$_{0.5}$ synthesized was well crystallized and possessed irregular elongated shape which is similar to the results reported by Liang *et al*. [10]. The synthesized Ni(BDC)(TED)$_{0.5}$ display nonuniform crystal size.
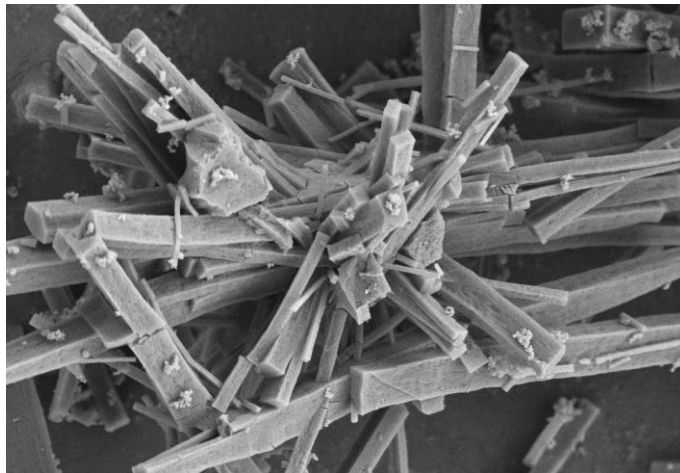

Figure 1 FESEM images of Ni(BDC)(TED)$_{0.5}$

Figure 2 shows FESEM top view images of the membranes. The fillers are observed as tiny white dots on the surface of MMMs. As the filler loading increased from 5 wt% to 20 wt%, the number of tiny white dots on the MMMs surface increased due to the presence of higher Ni(BDC)(TED)$_{0.5}$ loading in the MMMs as well as the one beneath the surface of MMMs [15]. Figure 3 shows the FESEM cross-sectional images of the membranes. The incorporation of Ni(BDC)(TED)$_{0.5}$ as the filler into the polymer matric disrupts the intermolecular chain packing of the polymer and induces

change on the morphology and structure of the membranes [16]. Besides, dispersion of filler in the MMMs was observed. The dispersion of the filler can be further indicated by the mapping of Ni element conducted on the cross section of the MMMs as shown in Figure 4. As the filler loading increased, the intensity of the purple dots increased.
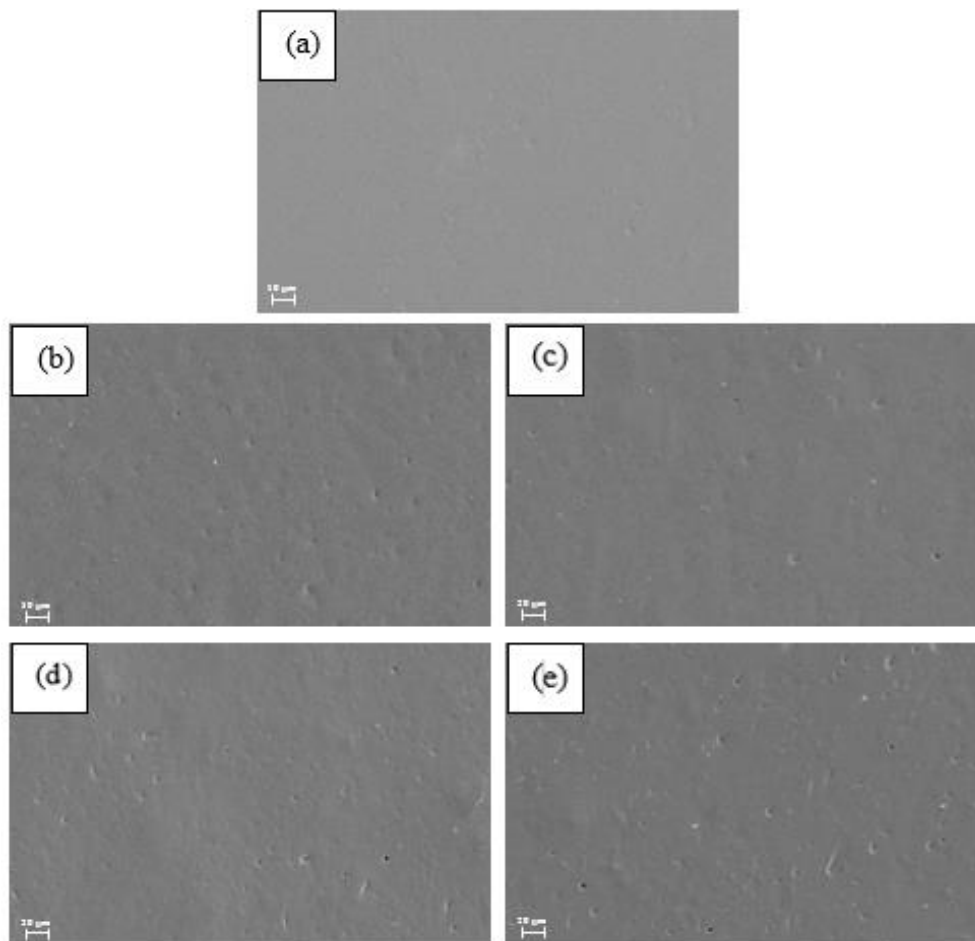

Figure 2 FESEM top view images of (a) Pristine Psf membrane, and MMMs incorporated with $Ni(BDC)(TED)_{0.5}$ loading of (b) 5 wt%, (c) 10 wt%, (d) 15 wt%, and (e) 20 wt%
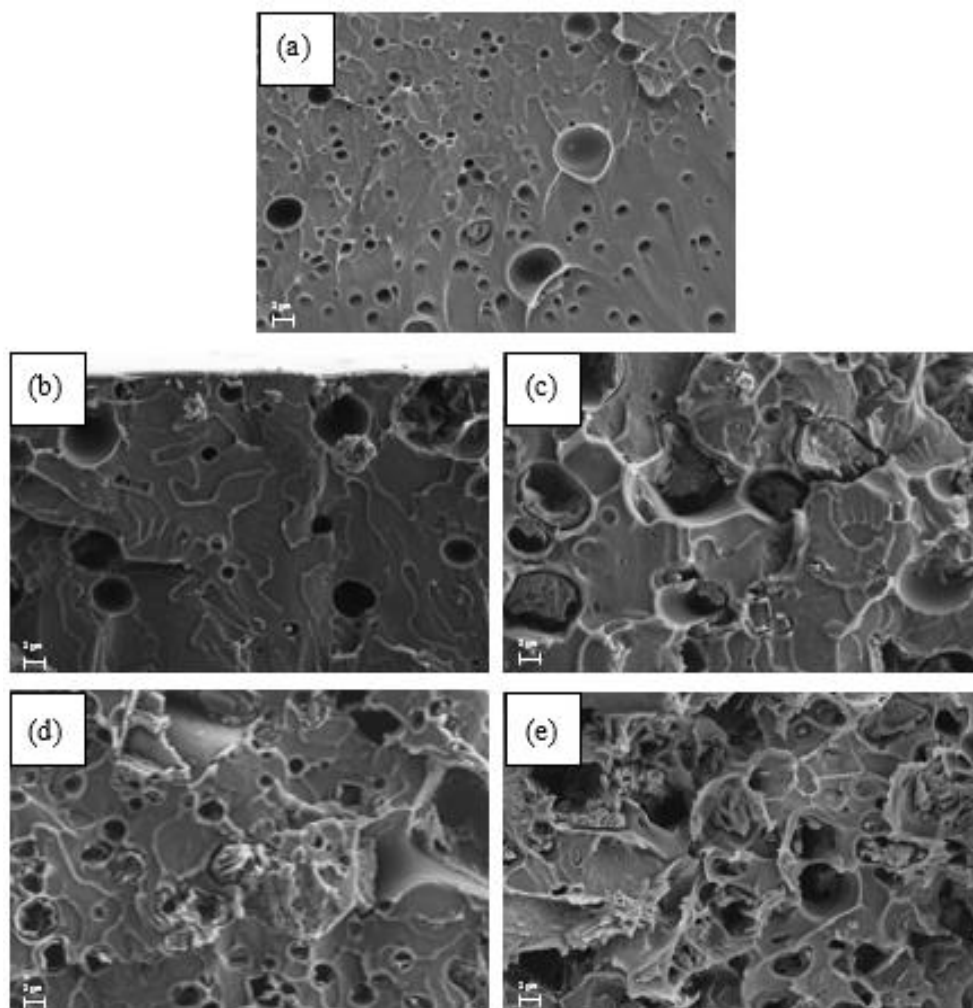
Figure 3 FESEM cross-sectional images of (a) Pristine Psf membrane, and MMMs incorporated with Ni(BDC)(TED)$_{0.5}$ loading of (b) 5 wt%, (c) 10 wt%, (d) 15 wt%, and (e) 20 wt%
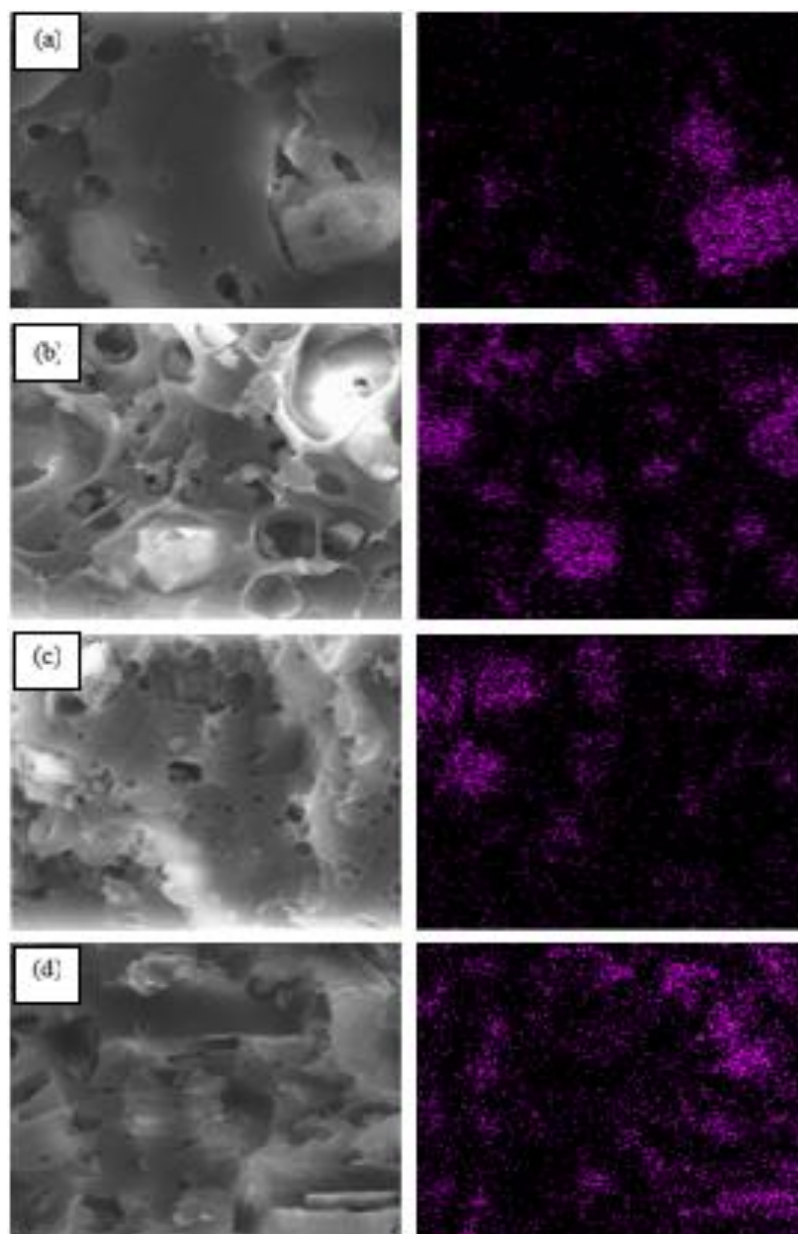
Figure 4 Mapping of Ni element on cross section of MMMs incorporated with Ni(BDC)(TED)$_{0.5}$ loading of (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt%

3.2 Crystallinity

Figure 5 shows the XRD pattern of Ni(BDC)(TED)$_{0.5}$ which exhibit main peaks at 2θ = 8.11°, 9.47°, 11.63°, 12.49° and 16.46°. All the XRD peaks displayed by the sample are in good agreement with the XRD patterns reported in the literature [9, 10, 17, 18]. The results obtained show that Ni(BDC)(TED)$_{0.5}$ was successfully synthesized through the solvothermal method under the synthesis temperature of 120 °C for 48 hours. The sharp and narrow peaks exhibited in the XRD patterns shows the high crystallinity of Ni(BDC)(TED)$_{0.5}$ synthesized in current project.

Figure 6 shows the XRD diffraction patterns of pristine Psf membrane and 20 wt% Ni(BDC)(TED)$_{0.5}$/Psf MMM. The diffractogram corresponding to the Ni(BDC)(TED)$_{0.5}$/Psf MMM is formed by characteristic Ni(BDC)(TED)$_{0.5}$ peaks

in addition to the XRD peak of Psf. The sharp peaks at 2θ of 8.85° and 16.23° was attributed to the filler present in the MMMs, whereas Psf was characterized by a reduced structural order, indicated by the presence of the broad peak at 2θ of 18.14°. This peak also appear at 2θ of 18.43° on the XRD pattern of pristine Psf membrane which is in good agreement with the literature reported by Ionita *et al.* [19], Cacho-Bailo *et al.* [20], and Murali *et al.* [21]. The results obtained show that Ni(BDC)(TED)$_{0.5}$ was successfully incorporated into the Psf polymer matrix to form MMMs.
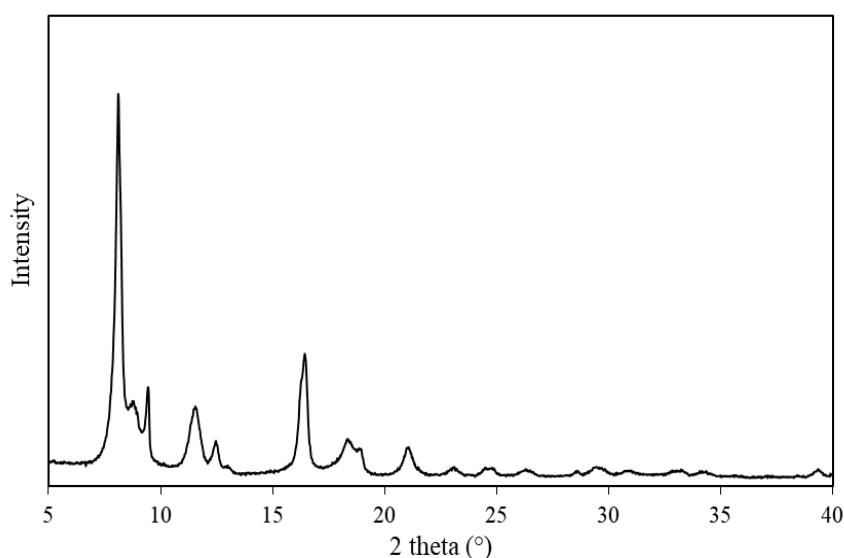
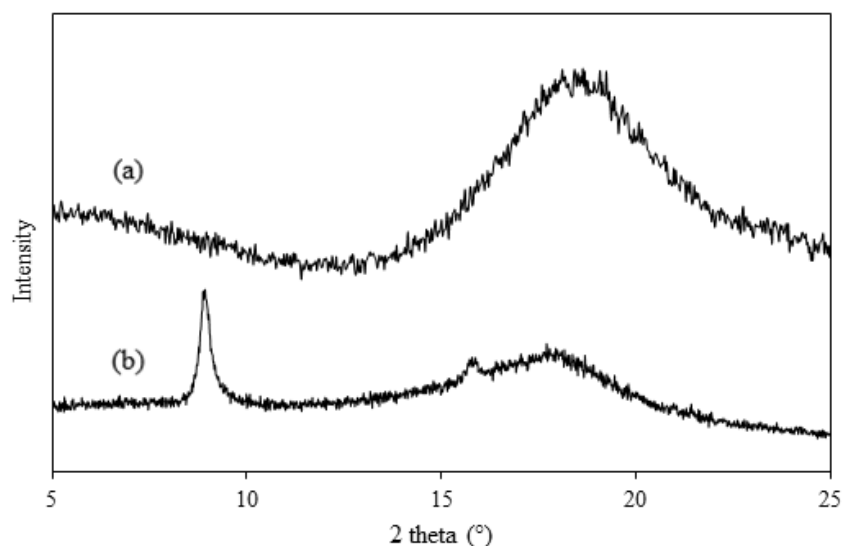

Figure 5 XRD diffraction pattern of Ni(BDC)(TED)$_{0.5}$

Figure 6 XRD diffraction patterns of (a) Pristine Psf membrane and (b) 20 wt% Ni(BDC)(TED)$_{0.5}$/Psf MMM

3.3 Gas Permeation Test

Figure 7 shows the result of CO_2 gas permeation and CO_2/CH_4 selectivity for pristine Psf membrane and MMMs incorporated with Ni(BDC)(TED)$_{0.5}$

loading of 5-20 wt%. As shown in Figure 7, the CO_2 gas permeances and CO_2/CH_4 selectivity increased when the filler loading in the MMMs was increased from 5 wt% to 10 wt%. This might be due to incorporation of $Ni(BDC)(TED)_{0.5}$ into the MMMs which result in stronger electrostatic interactions between the framework and CO_2 compared to CH_4. Chen *et al.* [22] reported higher CO_2 adsorption in $Zn(BDC)(TED)_{0.5}$ compared to CH_4 due to the stronger electrostatic interactions with the framework. However, it is observed that the CO_2 permeances increased in a more drastic manner and the CO_2/CH_4 selectivity started to decrease when the filler

loading was increased more than 10 wt %. This might be because of the more severe formation of voids that lead to the occurrence of leaky interface. Hence, CO_2 permeability increased but the CO_2/CH_4 selectivity was sacrificed [23]. Erucar and Keskin [24] predicted the CO_2/CH_4 selectivities of about 4-105 for different polymer matrixes incorporated with $Zn(BDC)(TED)_{0.5}$. Incorporation of 10wt % of $Ni(BDC)(TED)_{0.5}$ into MMMs in current study enabled achievement of optimum CO_2/CH_4 selectivity of 11.75, which is comparable with the lower range of CO_2/CH_4 selectivities predicted by Erucar and Keskin [24].
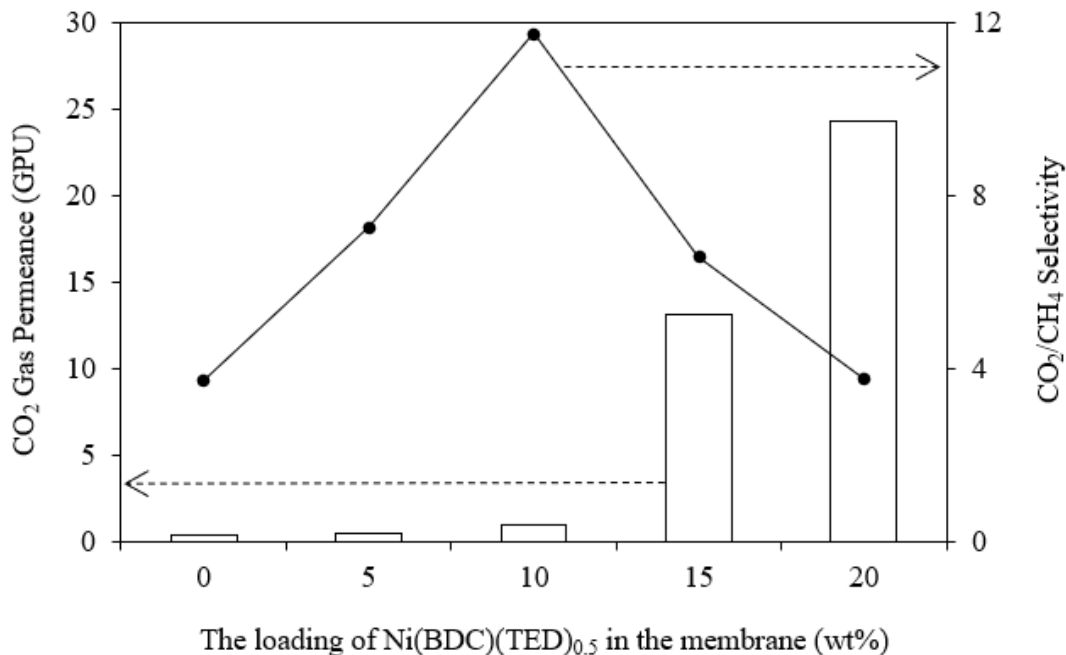

Figure 7 CO_2 gas permeance and CO_2/CH_4 selectivity of pristine Psf membrane and MMMs incorporated with different $Ni(BDC)(TED)_{0.5}$ loading

4.0 CONCLUSION

In the current study, the characterization results showed that the $Ni(BDC)(TED)_{0.5}$ was successfully synthesized via solvothermal method and it was successfully incorporated into Psf

polymer matrix. From FESEM analysis, $Ni(BDC)(TED)_{0.5}$ was well crystallized and possessed an irregular elongated shape. The incorporation of $Ni(BDC)(TED)_{0.5}$ as the filler into the polymer matric induced change on the morphology and structure of the membranes. From the gas permeation

test, the CO_2 permeances increased when the filler loading in the MMMs was increased from 5 wt% to 20 wt%. Whereas the CO_2 selectivity increased when the filler loading was increased from 5 wt% to 10 wt%, and then decreased when the filler loading was increased beyond 10 wt%. Optimum CO_2/CH_4 selectivity of 11.75 was obtained for MMMs loaded with 10 wt% of Ni(BDC)(TED)$_{0.5}$ in current study.

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