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FABRICATION OF ZIF-8 / POLYIMIDE MIXED MATRIX MEMBRANES AND THEIR STRUCTURAL PROPERTIES

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ABSTRACT

In the present research, a series of mixed matrix membranes (MMMs) consisting of 6FDA-durene as polyimide phase and ZIF-8 as inorganic filler were synthesized and characterized. The loading of ZIF-8 in the polyimide phase were varied from 5 to 20 wt%. The structural properties of the resultant membranes were studied using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX) Spectroscopy. The characterization results showed that excellent compatibility and good distribution of ZIF-8 in 6FDA-durene polyimide phase were observed even at higher ZIF-8 loading up to 20 wt%

Keywords: ZIF-8, 6FDA-durene mixed matrix membrane.

INTRODUCTION

Membrane gas separation technology has emerged rapidly since early of 1980s [1]. The attractiveness and ability of membrane in gas separation encourages the researchers to search for the membranes which offer cost benefits for both environmental and energy related processes [2]. Generally, membranes are fabricated using polymeric and inorganic materials. However, polymeric membranes demonstrate the restriction in terms of performance while inorganic membranes are costly and extremely difficult to produce [3].

Therefore, a satisfactory method to enhance the separation properties of membranes is developed by embedding dispersed solids such as zeolites and carbon molecular sieves into the membrane matrix. Mixed matrix membranes (MMMs) have been extensively studied by various researchers in the recent years because the incorporation of inorganic fillers into the polymer matrix can enhance the properties of a membrane material and at the same time, improve the separation performance [4].

Zeolitic imidazolate frameworks-8 (ZIF-8) is one of the most studied materials for gas separation due to its excellent chemical and hydrothermal stability, high surface area, and highly porous open framework structure [5]. ZIF-8 is formed by linking zinc (II) cations and 2-methylimidazole anions, giving a sodalite (SOD) zeolite type structure with two times larger of pore size compared to SOD zeolites. The existence of imidazole ligand in ZIF-8 enables the chemical interaction with CO_2 through non-covalent bond [6], therefore enhance the selectivity of ZIF-8 for CO_2/CH_4 separation.

Recently, ZIF-8 has emerged as attractive filler in the fabrication of mixed matrix membrane for the selective removal of CO_2. On the other hand, 6FDA-durene polyimide has been utilized by various researchers as polymer based mainly due to its overwhelming permeability and selectivity. Even though the incorporation of nano-sized filler in MMM has the potential to improve the separation properties, a defect-free MMM with homogenous distribution of fillers remains challenging. This is due to the difficulties in getting well dispersion of nano-sized inorganic filler in the polymer matrix and good compatibility between inorganic filler and polymer phase [7]. Moreover, the excess loading of the filler in the polymer matrix could enhance the formation of voids and thus, affect the properties and reduce the effectiveness of the membrane [8]. To date, researchers are still making a great effort in establishing a reliable method to fabricate defect-free MMM.

Therefore, in the present work, a series of MMMs were fabricated by incorporating different loadings of nano-sized ZIF-8 into 6FDA-durene polymer matrix. Contrary to the previously reported literature [9], the fabrication method of MMM was modified by prolonging the duration of ZIF-8 dispersion in the solvent and the inorganic filler loadings were further increased up to 20 wt%. The physical and chemical properties of the resultant membranes were characterized using different analytical tools such as XRD, FESEM and EDX.

METHODOLOGY

Chemicals

2, 3, 5, 6- Tetramethyl-p-phenylenediamine (durene diamine, 99% trace metal basis, Sigma Aldrich) monomers were purified by re-crystallization in methanol. 4, 4' – (Hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99% purity, Sigma Aldrich) monomers were purified by vacuum sublimation prior to use. N-methyl-2-pyrrolidone (NMP) was purified by using a vacuum distillation. Propionic anhydride (PA, ≥ 98% purity, Merck) and triethylamine (TEA, ≥ 99% purity, Merck) were used as received. Methanol (≥ 99.9% purity, Merck) and dichloromethane (DCM, ≥ 99.8% purity, Sigma Aldrich) solvent were used as received. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, > 98% purity, Sigma Aldrich) and 2-methylimidazole (Hmim, 98% purity, Sigma Aldrich), methanol (99.8% purity, Merck) were used without further purification.

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Preparation of 6FDA-durene

6FDA-durene polymer was synthesized using chemical imidization method reported by Liu *et al*. [10]. Equal mole of durene-diamine and 6FDA monomers were dissolved in purified NMP. The mixture was stirred for 24 h under nitrogen purge to obtain polyamic acid (PAA) solution. The mole ratio of propionic anhydride (PA) / triethylamine (TEA) to 6FDA of 4:1 were added to the PAA solution for chemical imidization. The polyimides were precipitated in methanol and then washed with methanol before dried at 150 °C in vacuum oven for 24 h.

Preparation of ZIF-8

ZIF-8 nanofiller is synthesized at room temperature by mixing zinc nitrate hexahydrate (Zn (NO3)2.6H2O) and 2-methylimidazole (2-MeIM) in methanol under stirring for 1 h [6]. The solution mixture was centrifuged at 7800 rpm for 5 minutes to recover the solid particles from milky colloidal solution. The solid was then washed with methanol for several times and dried in the oven at 60ºC for 24 h prior to use.

Preparation of pristine 6FDA-durene

6FDA-durene dense film was prepared by following the method as reported by Wijenayake *et al*. [11]. A 3% w/v solution of polymer in DCM was prepared and then cast on a Petri dish using a syringe through 1 µm filter. The cast film was dried in an oven at 60 °C for 24 h followed by another 24 h under vacuum. The oven temperature was increased from 60 to 250 °C at a heating rate of 25 °C/h before annealed at 250 °C for 24 h.

Preparation of pristine 6FDA-durene

MMMs with different inorganic fillers loadings were prepared by following the procedure as described by Askari and Chung [12]. The polymer and ZIF-8 solutions were prepared separately in two vials. 6FDA-durene polymer was added into DCM and stirred until dissolved to produce polymer solution. 5, 10, 15 and 20 wt% of ZIF-8 crystals were added to the DCM, stirred and sonicated for 3 h (alternating 30 min stirring followed by 30 min sonication) to disperse ZIF-8 in DCM. Sonication was done in an ultrasonication water bath operating at 120 W and 40 kHz. The polymer solution was added and the mixture was further stirred vigorously for 1 h. The mixture was then casted on a Petri dish.

Characterization of ZIF-8/6FDA-durene MMM

For ZIF-8 particles, X-ray diffraction (XRD) pattern of the sample was obtained using STOE Stadi-p diffractometer with CuKα radiation (λ=1.54059Å) in 2 theta range of 5-50º. In order to identify the morphology and crystal size of the particle, field emission scanning electron microscope (FESEM) was performed using SUPRA 50VP, Carl Zeiss Inc.

ZIF-8/6FDA-durene MMM was characterized by FESEM and EDX. Images of the cross section and the elemental compositions of the resultant membranes were obtained by using FESEM and EDX, respectively. Cross sections of the membranes were prepared by freeze-fracture after immersion in liquid nitrogen for several minutes. In addition, the elemental compositions of the fillers presence in the mixed matrix membrane were verified via the EDX mapping image and data analysis.

RESULTS AND DISCUSSION

Characterization of ZIF-8

The XRD pattern of ZIF-8 sample synthesized in the present work is shown in Figure-1. Referring to Figure-1, the XRD pattern was consistent with the reported XRD pattern for ZIF-8 by Cravillon *et al.,* confirming the formation of pure crystalline ZIF-8 phase [13]. The relative intensity and peak position of the ZIF-8 sample was in agreement with the XRD pattern reported by Lai *et al.* [6] with the peaks at 2θ = 7.30º, 10.36º, 12.68º, 16.40º and 17.98º. A sharp peak at 2θ of 7.30º was observed in the XRD pattern of the ZIF-8, indicating that a highly crystalline material was achieved. The low baseline and the absence of non-ZIF-8 peaks indicated that the products were free from impurities and no phase transformation occurred during the crystallization stage.

The morphological features of ZIF-8 crystals were investigated using FESEM and the images are shown in Figure-2. Based on Figure-2, the formation of well-shaped and rhombic dodecahedron crystals of ZIF-8 was obtained. This observation is similar with those images reported from the literature for ZIF-8 sample [14]. The average particle size of the synthesized ZIF-8 is 50 nm.

Characterization of pristine and MMM

Figure-1 demonstrates the XRD pattern for ZIF-8 crystal, pristine membrane and 5% ZIF-8/6FDA-durene MMM. Peaks at 2θ values of 7.30º, and 12.68º were observed in the XRD pattern of 5% ZIF-8/6FDA-durene MMM which confirmed the presence of ZIF-8 in the resultant MMM.

Figure-3 displays the cross section morphology of pristine and ZIF-8/6FDA-durene MMM. Referring to Figure-3, ZIF-8 particles showed good compatibility between the particle and polymer phase [15].

All the resultant membranes demonstrated well distribution of ZIF-8 particles in the polymer matrix and no indication of filler agglomeration was observed. It can be interpreted that ZIF-8 particles were well dispersed during the MMM fabrication.

The elemental analysis of pristine 6FDA-durene and 5% ZIF-8/6FDA-durene MMM was verified using EDX. The analysis showed that the pristine 6FDA-durene membrane consists of C, F, O, N elements with the average atomic percent of 57.64%, 14.70%, 11.40% and 16.27%, respectively. While, the elements of Zn with atomic percent of 0.07% were detected in ZIF-8/6FDA-durene membrane, which further confirmed the present of ZIF-8 in the polymer phase. The dispersion of ZIF-8 particles in MMM is verified by mapping the Zn element using EDX.

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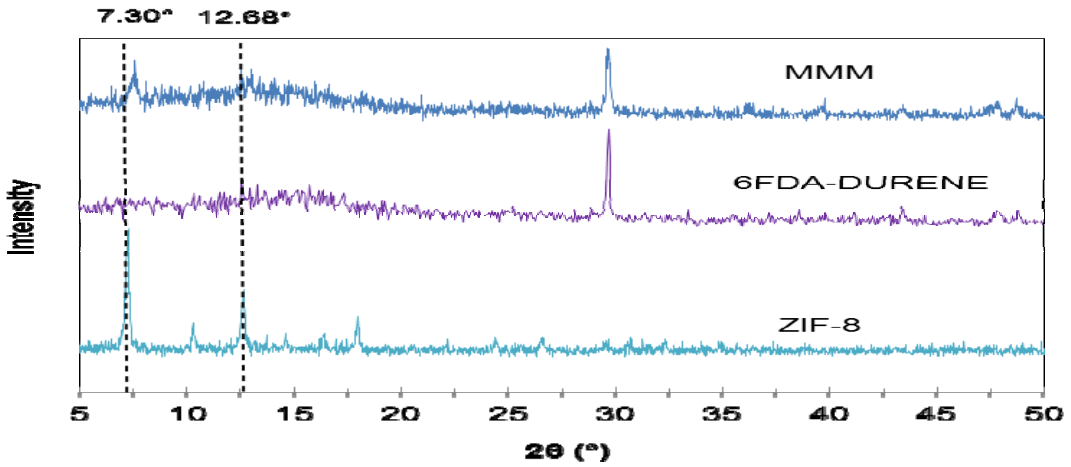

Figure-1. XRD pattern of ZIF-8 crystals, pristine 6FDA-Durene and ZIF-8/6FDA-Durene mixed matrix membranes.

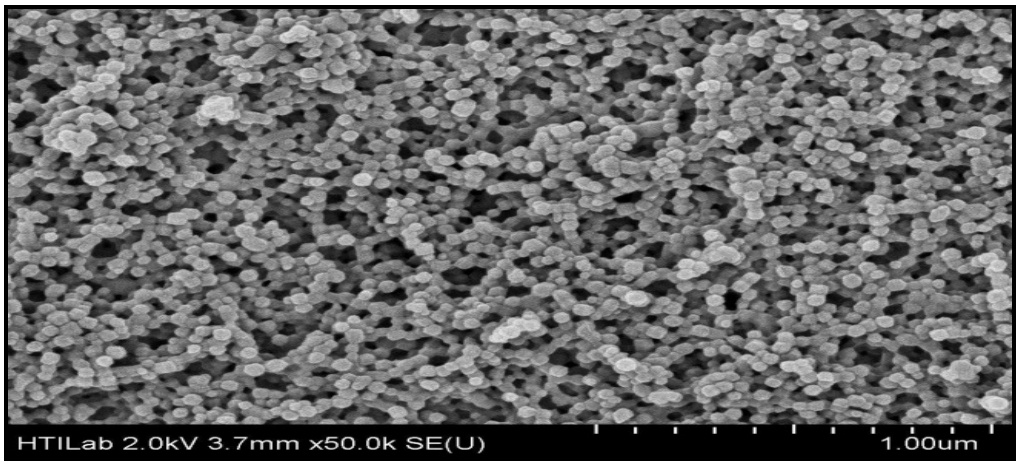

Figure-2. FESEM image of ZIF-8 nanocrystals.

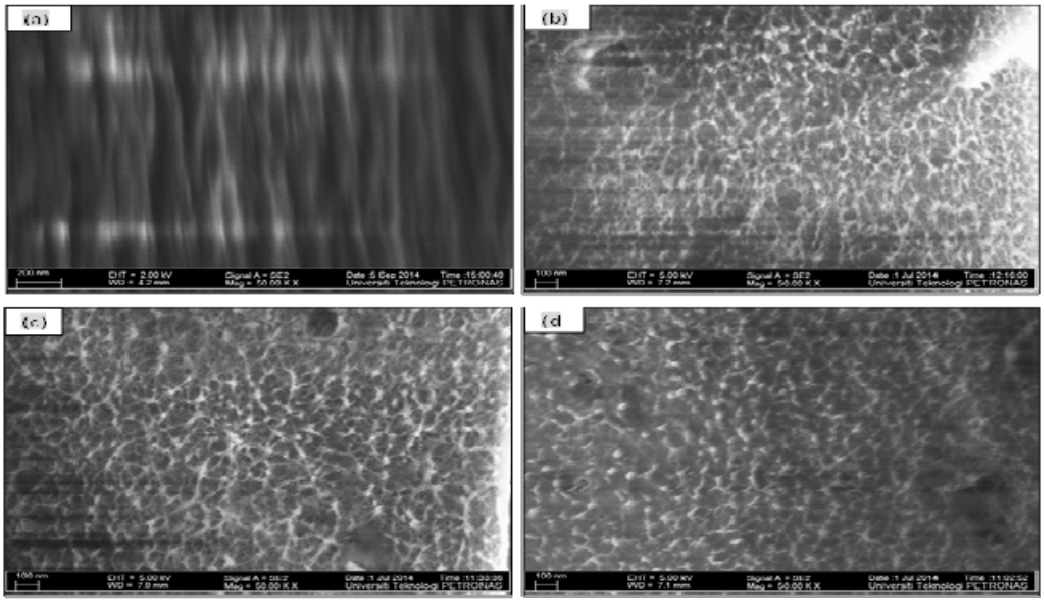

Figure-3. FESEM images of ZIF-8/6FDA-Durene mixed matrix membranes (a) 0wt% (b) 10wt% (c) 15wt% (d) 20wt%.

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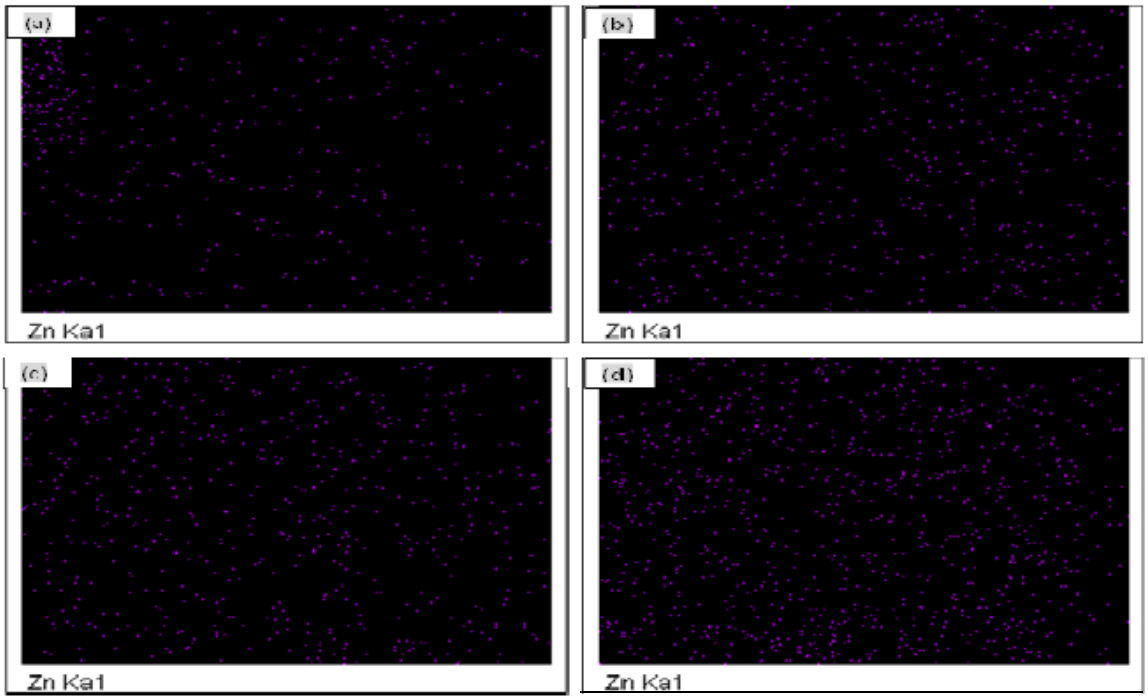

Figure-4. EDX mapping of ZIF-8/6FDA-durene MMM at different loading percentage (a) 5 wt% (b) 10 wt% (c) 15 wt% and (d) 20 wt%.

Figure-4 shows no agglomeration of ZIF-8 in the polymer matrix at loading of 5, 10, 15 and 20 wt% from the EDX images. The fabrication of MMM in this work successfully improved the distribution and dispersion of particles in polymer phase as compared to our previous reported data [9].

CONCLUSIONS

In this work, ZIF-8 and ZIF-8 /6FDA-durene MMM were prepared. XRD result confirmed the formation of ZIF-8 structure. FESEM images showed that well-shaped and rhombic dodecahedron crystals of ZIF-8 with average particle size of 50 nm were formed. ZIF-8 /6FDA-durene membranes were fabricated by incorporation of 5, 10, 15 and 20 wt% of ZIF-8 into 6FDA-durene polymer matrix. FESEM images demonstrated that the resultant membranes exhibited good compatibility between ZIF-8 particles and polymer phase. Well dispersion of particles with no sign of agglomeration was observed in EDX mapping images. The fabrication method of MMM reported in this work has been improved as compared to our previous reported study mainly due to the modification of the fabrication technique during MMM formation. Therefore, the present work proved that the fabrication parameters play a major role in the preparation of MMM with minimum defects level.

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