Synthesis and characterization of polyester thin film composite membrane via interfacial polymerization: Fouling behaviour of uncharged solute

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Abstract. Most hydrolysis studies on biomass in Malaysia produce high amount of xylose and glucose compared to other monosaccharides and most of them are acidic. Thin film composite (TFC) membrane developed via interfacial polymerization using triethanolamine (TEOA) and trimesoyl chloride (TMC) as monomers allows separation at low pH to occur without damaging its performance. Comparative studies were carried out on membranes with and without the thin film layer formed via interfacial polymerization on the polyethersulfone (PES) support. The surfaces of the membranes were characterized by field emission scanning electronic microscopy (FESEM), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and hydrophilicity via contact angle measurement. In addition, the performance and uncharged solute fouling behaviour of TFC membrane were also investigated. The TFC membrane used for characterization purposes was prepared at TEOA concentration of 4 % w/v in 1 \times 10^{-6} M sodium hydroxide solution, TMC concentration of 0.25 % w/v in pure hexane, reaction time of 45 minutes, and cured at temperature of 60 °C. Characterization results showed a huge different between the synthesized TFC membrane and the un-synthesized PES membrane in term of surface properties and morphology. Nanofiltration results indicate that the formation of thin layer on top of PES support membrane improved the separation performance compared to PES support membrane. The synthesised polyester TFC membrane have irreversible fouling of 11.02 (±5.60) % and reversible fouling of 5.59 % using water as cleaning agent.

1. Introduction

Surface chemistry and morphology of membrane are greatly influence the transmembrane transport of components as well as on the efficiency of the membrane process [1]. Thus, surface modification of previously formed membranes is a promising approach to confer new properties to the existing membranes providing surfaces with tailor-made separation properties, energies and chemical functionalities [2]. The emerging of this asymmetric composite membrane also known as TFC membrane has changed the membrane industry significantly. TFC membranes are synthesized by first fabricating the asymmetric membranes and then coat another ultrathin barrier layer on top of the fabricated membranes. The coating techniques that had been introduced were interfacial polymerization, grafting polymerization, and layer-by-layer deposition [3,4]. Although a lot of effort has been put in developing membrane using grafting polymerization, a relatively small number of grafted polymeric materials found their way in commercial and large-scale applications [5]. Layer-by-layer deposition membranes have superiority over the other two fabrication techniques, but not practical in term of real applications where almost all studies are still conducted in lab scale [6]. Besides, most commercial TFC RO and NF membranes were fabricated through IP. IP allows the properties of top and bottom layer to be controlled independently, has pave ways to a wide variety of TFC membranes [3].
Interfacial polymerization techniques gained popularity over the other coating techniques when a variety of TFC membrane was successfully developed by many companies, allowing wide application in the separation processes industry. Interfacial polymerization technique allows properties of both bottom support and top barrier film to be individually tailored and optimized to achieve desired separation selectivity and rate [4]. Only few works have carried out interfacial polymerization technique to prepare other polymeric thin-film polyester membranes in comparison to thin-film polyamide membranes [2]. Polyester RO membrane synthesized by Kwak et al. [7] had water permeate flux eleven times higher than that of polyamide membrane. In addition, the incorporation of ester linkage increased the oxidation resistance of the membrane which has significantly increased the membrane tolerance on chlorine attack [2]. In recent years, many studies focused on the preparation of TFC membranes using interfacial polymerization technique with monomers having special functional groups [8].

Tang et al. [9] had utilized TEOA, an economical monomer in enhancing the performance of the thin-film composite membrane. TEOA belong to the tertiary amino group, where its molecules can be flexibly transferred into quaternary ammonium group through variation of feed pH. The changes on the membrane surface also increases membrane hydrophilicity at lower pH feed [9,10].

TFC membranes are susceptible to fouling. After a long period of academic and industrial researches, it is generally accepted that hydrophilicity, surface charge, and surface roughness of the TFC membrane surface are the major factors which affect the membrane susceptibility to fouling [1]. Membrane fouling is the accumulation of substances on membrane surface and/or within membrane pores, which causes a reduction in permeate flux (i.e., flow of water through membrane) with time for constant pressure filtration, or an increase in trans-membrane pressure with time for constant permeate flux filtration [11]. Membrane fouling classified into reversible fouling and irreversible fouling. The former can be cancelled by physical means of cleaning, whereas the latter needs chemical cleaning to be cancelled [12].

This work aims to prepare, characterize, and compare the characteristics of synthesized polyester TFC membrane via interfacial polymerization with its initial state (PES membrane). In addition, this works also add information on the xylose and glucose fouling behaviour of polyester TFC membrane. The synthesis parameters used in this work were based the best condition found in our previous study [13].

2. Experimental
2.1 Materials
The polyethersulfone membrane was purchased from AMFOR Inc. (China) with the commercial name of UF PES50. The membrane has a nominal molecular weight cut-off of 50 kDa, and water flux of 260 LMH at 25 °C and 50 psi. The chemicals used in this study were triethanolamine (R & M Marketing, Essex, UK), tri-mesoyl chloride (Alfa Aesar, UK), sodium hydroxide (Merck, Germany), n-hexane (Merck, Germany), xylose (Sigma Aldrich, USA), glucose (Sigma Aldrich, USA), and acetonenitrile (J.T. Baker, USA). All chemicals were analytical grade with high purity (> 99%) and acetonitrile with High Performance Liquid Chromatography (HPLC) grade.

2.2 Preparation of TFC membrane
The polyester thin film composite membrane was prepared based on previous studies [9,10,14] with slight modification in the preparation of aqueous phase solution. The aqueous phase solution composed of 4 % w/v TEOA in 1 x 10^{-6} M sodium hydroxide aqueous solution. The organic phase solution was prepared by dissolving 0.25 % w/v of TMC in pure hexane. PES support membrane was first immersed in aqueous phase solution for a period of 30 minutes. After that, the membrane was then drained and rolled with a glass rod to remove excess liquid. Then, the membrane was immersed in the organic phase solution for a period of 45 minutes. The polyester thin film composite membrane was cured at a temperature of 60 °C for 30 minutes.
2.3 Membrane characterization (Field emission scanning electron microscope (FESEM), Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, Contact angle measurement)
The morphology of membrane surface was examined by FESEM equipment (Model JSM-6330F, JEOL, Japan). The membrane surface was examined by sticking the membrane on top of the support with carbon tape. All the membranes were coated with platinum under vacuum.

ATR-FTIR spectra were obtained using a Thermo Scientific Nicolet iS-10 FT-IR spectrometer equipped with Attenuated Total Reflection (ATR) element of Smart iTX AR Diamond and an Omnic 5.1 software. The membrane active layers were pressed tightly against the crystal plate. The TFC membrane, PES membrane, TEOA and TMC were analysed, with each spectrum averaged from 256 scans collected from 650 to 4000 cm\(^{-1}\) at 2 cm\(^{-1}\) resolution. The experiments run with air as the background and no baseline or ATR corrections were applied.

The hydrophilicity of all the membranes were measured using contact angle goniometer (JY-82, Chengde testing machine Co. Ltd., China) using the sessile drop method. A glass slide was immersed in pure ethanol for 10 min, rinsed with ultrapure water and then dried before being used as an inert flat surface. Membrane was then placed on top of the glass slide and clipped making sure the surface of membrane is parallel to the glass flat surface. A droplet of 5 μL of ultrapure water at the end of ‘1’-shaped needle was carefully deposited to membrane surface to avoid the effect of falling force by gravity. A static image of the droplet in equilibration with the membrane surface was taken. Later, image analysis and contact angle computation were performed using the analysis software. For ensuring the accuracy, the measurements were performed at five different locations, and then the average value was regard as the final contact angle result.

2.4 Nanofiltration set-up and fouling test
A Millipore stirred cell (Model 8200, Millipore-Amicon Corporation, USA) having a maximum volume uptake of 200 mL and an effective membrane area of \(2.87 \times 10^{-3} \text{ m}^2\) was used in all experiments. Prepared TFC membrane and virgin PES membrane was fitted into the membrane holder at the bottom of the stirred cell. Other parts are then assembled together and place on top of a magnetic stirrer (Model MS-20D, Daihan Scientific Co. Ltd., South Korea).

The fouling experiment was conducted according to the following procedure: (a) pre-compaction of the membrane with ultrapure water at 4 bar for 10 minute to stabilize the pressure-induced membrane deformation; (b) filtration of the ultrapure water to determine initial water flux, \(J_0\) for fouling index calculation by measuring mass of permeate collected at 4 bar and stirring speed of 300 rpm in 1 hour; (c) filtration of 180 mL of model sugar solution (1 % w/v of both xylose and glucose at ratio 1:1) at 4 bar for 6 hour and stirring speed of 300 rpm, where mass of permeate collected every 20 minute for normalized flux calculation; (d) cleaning of membrane with ultrapure water with stirring speed of 350 rpm for 30 minute without applying pressure to remove weakly adsorbed solutes on membrane surface; (e) filtration of the ultrapure water to determine final water flux, \(J_f\) for fouling index calculation by measuring mass of permeate collected at 4 bar for 1 hour and stirring speed of 300 rpm. All the mass observed in this experiment is converted to volume using density of water at 25 °C. The fouling of membrane was measured using relative flux reduction (RFR) and normalized relative flux (NRF). RFR is a measure of irreversible fouling calculated using Eq. 1. NRF demonstrates the fouling trend during filtration calculated using Eq. 2 where \(J_0\) is the pure water flux before filtration (Lm\(^{-2}\)h\(^{-1}\)), \(J_f\) the pure water flux after filtration (Lm\(^{-2}\)h\(^{-1}\)) and \(J_t\) is the permeate flux at time \(t\) (Lm\(^{-2}\)h\(^{-1}\)).

\[
RFR = \left(1 - \frac{J_f}{J_0}\right) \times 100\%
\]  
(1)

\[
NRF = \frac{J_t}{J_0}
\]  
(2)
3. Results and Discussion

3.1 Membrane characterizations

The membrane was characterized using ATR-FTIR spectroscopy to analyse the surface chemistry of support PES membrane before and after interfacial polymerization between TEOA and TMC. Figure 1 showed spectra belonging to virgin PES membrane and freshly prepared TFC membrane. A strong peak at wavenumber 1724 cm\(^{-1}\) was seen in the spectra of TFC membrane (Figure 1 (a)) beside the typical PES bands (Figure 1 (b)). This peak falls into the band belonging to a functional group of ester (\(C = O\) stretch) \([2,6]\). TFC membranes developed using TEOA and TMC in the past were particularly suitable for treating acidic feeds due to the formation of polyester thin-layer \([9,10]\).

![Figure 1. ATR-FTIR Spectra for (a) PES and (b) TFC membrane](image)

FESEM analysis was performed to observe the morphology of the support PES membrane surface after undergo interfacial polymerization to become TFC membrane. Figure 2 shows the FESEM surface images of both PES and TFC membrane at 5,000x magnification. The surface of TFC membrane in Figure 2 (b) spotted a “ridge and valley” structure, which were identical to previous studies \([9,13]\) which also synthesized polyester membrane from TEOA and TMC monomer. A distinct different of surface roughness and morphology can be seen from both images, between Figure 1 (a) and (b) proved that there was the formation of TFC layer on top of the support PES membrane by interfacial polymerization.

![Figure 2. FESEM for (a) support PES and (b) TFC membrane at 5,000x magnification](image)

The contact angle for support PES membrane was 51.03 ± 3.68 ° and TFC membrane was 30.08 ±1.27 ° as shown in Figure 3. TFC membrane has smaller contact angle than the PES implying that formation of polyester increases the hydrophilicity of the membrane, although the surface of membrane...
become rougher. Past studies [15,16] point out hydrophilic compounds such as xylose can easily pass through the membrane due to hydrophilic-hydrophobic interaction between membrane and compounds. Commercial membrane with better hydrophilic surface or lower contact angle also have been reported to have higher xylose separation factor [17].

![Figure 3. Contact angle for support PES and TFC membrane](image)

3.2 Fouling behaviour
The flux reduction over 6 hours (360 minutes) filtration time was observed as illustrated in Figure 4, where the NRF after a course of this filtration was 16.61 (±3.53) %. The TFC membrane has RFR of 11.02 (±5.60) % which represent the irreversible fouling. A reversible fouling of 5.59 % can be obtained after cleaning with ultrapure water. From Figure 4, it can clearly see that the rate of fouling was less severe compared to fouling of humic acid in previous study [10]. The fouling observed in this study is in good agreement with commercial membrane [18] where fouling of sugar was less susceptible in operations under 2 days.

![Figure 4. NRF during nanofiltration of model sugar solution](image)

4. Conclusion
The formation of polyester thin layer on top of polyethersulfone membrane were successfully verified using ATR-FTIR and FESEM analysis. The polyester thin layer formed altered the surface of the membrane from smooth and homogeneous to rough surface with “ridge and valley” structure. The formed polyester thin layer not only altered the morphology of the membrane surface but improved the hydrophilicity of the surface itself, which can be verified by contact angle measurement. Besides, the synthesised membrane has less severe fouling rate of xylose and glucose.
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