

Synthesis And Performance Of Thin Film Composite Nanofiltration Polyester Membrane For Removal Of Natural Organic Matter Substances

N.A. Jalanni

M .N. Abu Seman*

C. K. M Faizal

Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak 26300 Gambang Kuantan Pahang, Malaysia

**e-mail: mazrul@ump.edu.my*

Nanofiltration (NF) polyester thin-film composite (TFC) membranes have been prepared by interfacial polymerization using commercial polyethersulfone membrane support. At 6% (w/v) triethanolamine (TEAO) concentrations in the aqueous solution and a range of interfacial polymerization times in the organic solution containing trimesoyl chloride (TMC) were studied. Nanofiltration membranes were produced with varying properties through interfacial polymerization technique. The ability to use NF membranes with varying properties will improve overall process efficiency. This study has shown that through interfacial polymerization technique, the variation of reaction time as well as can affect the performance of the membrane produced. As a result, increasing the reaction time resulted in decreasing water permeabilities. Polyester with some amide group produced after interfacial polymerization occurred as shown by FT-IR spectra. Straight lines were obtained between J_w and ΔP and the water flux of distilled water shown that flux is directly proportional to transmembrane pressure (TMP). At low reaction time (5 min), the water flux has no significant effect on water permeance. So, the reaction time has a significant effect on the growth of thin film.

Keyword: Nanofiltration, Thin-Film Composite, Characteristics, Humic Acid.

INTRODUCTION

Previous type of monomer that had been used of producing membrane comes from Bisphenol-A (BPA) as a monomer (Semman et al. 2010, Mohammad et al. 2003, Jayarani and Kulkarni 2000). Toxicity is the major problem of using BPA regarding human

health. Manufacturers used polycarbonate plastic as material for many baby bottles because it is rigid, shatter resistant and clear in color. Plastic baby bottles have received many attentions recently as research came to light showing many famous models leach BPA, a suspected endocrine disruptor (Beverly 2011). But there are safe

alternatives by using triethanolamine (TEOA) as monomer. The application of nanofiltration (NF) in drinking water treatment for various types of source water such as soft and hard surface waters have many common features. In all these NF applications, natural organic matters (NOM) are a potential fouling agent for the membranes and the major efforts to secure good practice in the plants.

However, it is particularly important to prepare thin film composite (TFC) membrane for the purpose of practicality and easy realization. Thus, it is natural to seek an inexpensive monomer to manufacture a new membrane whose property spectrum has the optimum cost performance balance for application. Tang et al (2008) found that triethanolamine (TEOA) is an active monomer which is environment-friendly, economical and easy to be obtained. And it can react with multifunctional acid chloride to form cross-linked network structure due to the existence of multi-hydroxyl in its molecule (Tang et al. 2008)

BPA polymer molecules are linked by ester bonds that are intent to hydrolysis when exposed to high temperatures or to acidic or basic substances (Welshons et al. 2006). Researchers have shown that BPA can leach out from polycarbonate plastics and from epoxy resins and other products in contact with food and drink, and as a result, routine ingestion of BPA is presumed (Vandenberg et al. 2007). The interfacial polymerization (IP) process is based on the reaction of two monomers in a two phase system, where the polymerization takes place in the interface between the two phases. In many cases the two monomers

consist of a polyfunctional amine and an acid chloride, dissolved in an aqueous and an organic phase, respectively. IP is widely used and researched, especially regarding the production of thin film composite (TFC) membranes (Cadotte et al. 1981).

Humic substances adversely affect the quality of drinking water since they impart colour and serve as precursors for the development of chlorinated compounds (Mamba et al. 2007). They also have complexing properties that include association with toxic elements and micro-pollutants (Wuilloud et al. 2003). Other authors (Siddiqui 2000, Albozfar et al. 1998) also suggest NF as an efficient and reliable process for natural organic matters (NOM) removal. The major problem in use of membrane processes for NOM removal is the requirement for pre-treatment in order to prevent fouling of the membrane. Fouling occurs mostly due to colloidal and scales precipitation as well as microbial growth. Humic substances are considered as a series of relatively high-molecular weight, brown to black coloured substances formed by secondary synthesis reactions. A humic acid are not soluble in water under acidic conditions ($\text{pH} < 2$) but is soluble at higher pH values.

EXPERIMENTAL

Materials

The polyethersulphone was supplied by the Solvay Plastics (Georgia). Triethanolamine (TEOA) purchased from R & M Marketing (Essex, UK) was used as an active monomer of aqueous phase. Sodium hydroxide (NaOH) was used to mix with TEOA purchased from Merck (Germany).

Trimesoyl chloride (TMC) used as an active monomer of organic phase was obtained from Alfa Aesar (UK). N-hexane was used as the organic phase solvent, which was obtained from Merck (Germany). Humic acid was purchased from Sigma Aldrich (Switzerland). For membrane preservation, glycerol and sodium disulphite that purchased from R & M Marketing (Essex,UK).

Membrane Preparation

The composite membranes were prepared by conventional interfacial polymerization technology. The typical, simple process used in this study was as follows. Membrane support was made by polyethersulfone (PES) and polyvinylpyrrolidone (PVP) as polymer and additive, respectively, with the N-methyl-2-pyrrolidone (NMP) as the solvent. Active monomer layer obtained through interfacial polymerization with aqueous phase and organic phase solution. Sodium Hydroxide (NaOH) used as base for TEOA.

A dope solution prepared by mixing 18% wt of polyethersulfone (PES) and 15%wt polyvinylpyrrolidone (PVP) dissolved with N-methyl-2-pyrrolidone (NMP) solvent. PES and PVP must mix well before added into solvent. This solution prepared by mixing PES and PVP powder in (NMP) solvent at certain speed (300rpm). Mixing process was done in the 250 ml volumetric flask that contained PES/NMP/PVP at right ratio as mentioned earlier. Then, the volumetric flask was slowly heated and stirred to speed up the dissolution process. While mixing process using the stirrer, the volumetric flask must wrap with aluminium foil to avoid the

solvent evaporate. After a few hours a yellowish solution like honey was obtained with many bubble gases appears. This solution need to be left for a few hours in the ultrasonic water bath at certain temperature until all air bubbles disappear. This step is really important to avoid the leakage of membrane while casting process. After solution clear from air bubbles, certain amount of solution was pour on the glass plate at room temperature and scatter it using doctor blade with 0.25mm opening. Gently and speedily, the liquid film on the glass plate soaked into water bath. This dope film converts to white opaque because of PES precipitation. Within 1 to 2 minutes, the film automatically peels off from the glass plate. The membrane rinsed with distilled water to remove excess solvent and then stored in the distilled water overnight.

Interfacial polymerization

Sodium Hydroxide (NaOH) solution with concentration 1% w/v prepared by dissolving 10g NaOH in 1000 ml distilled water and used as base medium for TEOA solution. Aqueous TEOA solution with concentration 6% w/v was prepared by dissolved 6 g TEOA in 100 ml NaOH aqueous solution, (NaOH 1% w/v). On the other hand, organic Trimesoyl Chloride (TMC) solution with concentration 0.15% w/v prepared in organic phase form by dissolved 0.15 g TMC in 100 ml n-hexane. Polyethersulfone (PES) supporting membrane was cut into a disc forms and immerse into aqueous TEOA solution (6% w/v) for 30 minutes. Then, the excess TEOA solution on the membrane surface was drained at room temperature about 2 minutes. After that, the TEOA coated membrane was immersed in

TMC-hexane for 5 minutes for interfacial polymerization purpose. The resulting aromatic composite polyester membrane was dried overnight at room temperature. Three membrane samples were produced at three different reaction times (5, 10 and 15 minutes).

Nanofiltration experiments

Before all NF experiments, each membrane was first immersed in distilled water and then placed in the filtration cell about one hour and pressurized at 400kPa for at least 10 minutes using distilled water. Subsequently, pure water experiments were conducted at 100-400 kPa to obtain water flux.

A stock aqueous solution of 15 mg/L humic acid was prepared using distilled water and adjusting the pH to a value slightly higher than 9 in order to make sure that all humic acid powder was completely dissolved. In this study, the humic acid feed solution pH was adjusted using 0.1M NaOH or 0.1MHCl and Hanna instruments pH 211 microprocessor pH meter was used.

Hitachi Ratio Beam Spectrophotometer (U-1800) at a wavelength of 254nm with Hellma 10mm cell made of Quartz SUPRASIL was used to determine the initial and final concentration of humic acid while filtration conducted. As the spectrophotometer detector reads the concentration in absorbance unit, a calibration curve using different standard solutions containing different concentrations of humic acid was determined. After pure water experiments, humic acid aqueous feed solution of 15 mg/L and pH 10 was used and the permeate flux (J) as well as the rejection were determined.

Membrane characterization

Chemical characterization of the membrane surface was accomplished by Fourier Transform Infrared (FT-IR) spectroscopy instrument with Thermo Nicolet Avatar 370 Fourier transform infrared spectrometer. Dry specimens of the membrane samples were cut to small size and mounted in FT-IR plate. The uncoated and TFC membranes were characterized with transmission FT-IR and the spectra were collected at spectral resolution of 4 cm^{-1} by accumulating 128 scans. The measured wave number range was 4000–650 cm^{-1} . All original spectra were baseline corrected using the Omnic 5.1 software.

RESULTS AND DISCUSSIONS

Both the uncoated and coated membranes were characterized by FTIR. Figure 2a shows the spectra of the coated membrane with 6% (w/v) TEOA at 5 min reaction time compared to the spectra of the uncoated membrane (Figure 2b). The reaction between the monomer TEOA in NaOH (pH = 10) and TMC in hexane, acting as organic phase, produces polyester polymer layer on membrane surface as explained in Figure 1. The results are demonstrated in Figure 2b, which indicate that the interfacial polymerization has occurred since two strong bands at 1150.97 cm^{-1} , 1105.80 cm^{-1} and 1240.53 cm^{-1} that correspond to ester(C-O), ester(C-O) and amine (C-N), respectively (Silverstein et al. 1981). As can be seen in Figure 2b, it is clearly shown that a new peak at 3377.69 cm^{-1} band was observed that indicated hydroxyl (-OH) stretch mode of carboxylic

group of the TMC (Ahmad and Ooi 2005).

Pure water flux (J_w) was measured for both the coated and uncoated membranes at different operating pressures, ΔP . Straight lines were obtained between J_w and ΔP and the water permeability, P_m , was determined from the gradient of the straight line in Figure 3. Figure 3 shows the water flux of the uncoated and TFC membranes prepared with monomer concentrations (6%, w/v) as a function of different the reaction times (5, 10, 15 minutes). The TFC membranes were named hereafter as M6-5, M6-10 and M6-15, respectively. It was found that the water flux of the TFC membranes decreased with increasing the interfacial polymerization reaction time. At low reaction time (5 min), the water flux has no significant effect on water permeability as compared to uncoated one. However, as the reaction time increased, the permeability was decreased up to 0.528 L/m².h.bar. The similar result also observed by Tang et al (2008) where they found that a significant decrease in the pure water flux only occurred when the reaction time applied was longer than 6 min. It is worth noting that all TFC membranes exhibited smaller permeate fluxes than the uncoated membrane. This is attributed to the formed denser layer or thicker layer of polyester formed on the membrane surface. Similar results also observed by Tang et al. (2008) and Abu Seman et al (2010). It was claimed that the reaction time have significant effect on the growth of thin film. In our case, as the TEOA concentration was increased, the thin-film composite layer was expected to be thicker resulting in membranes with lower permeabilities.

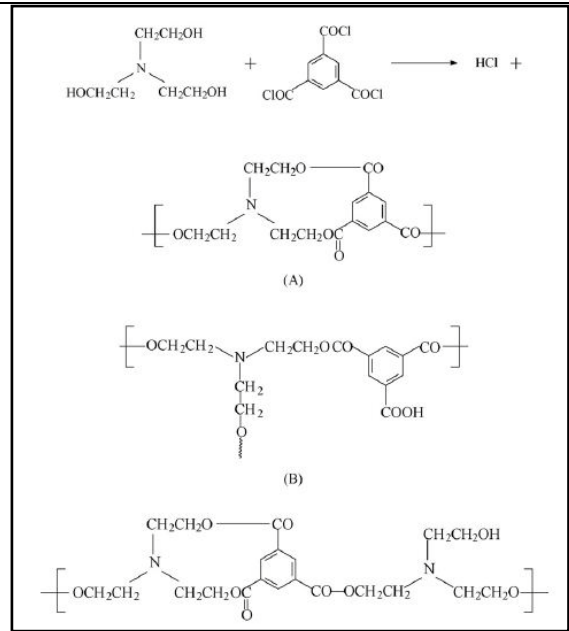
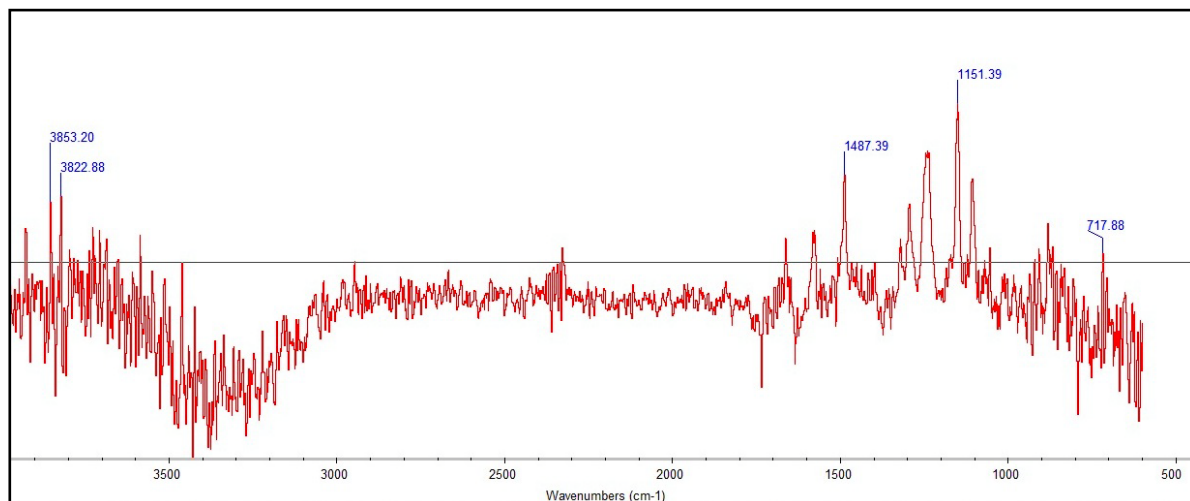
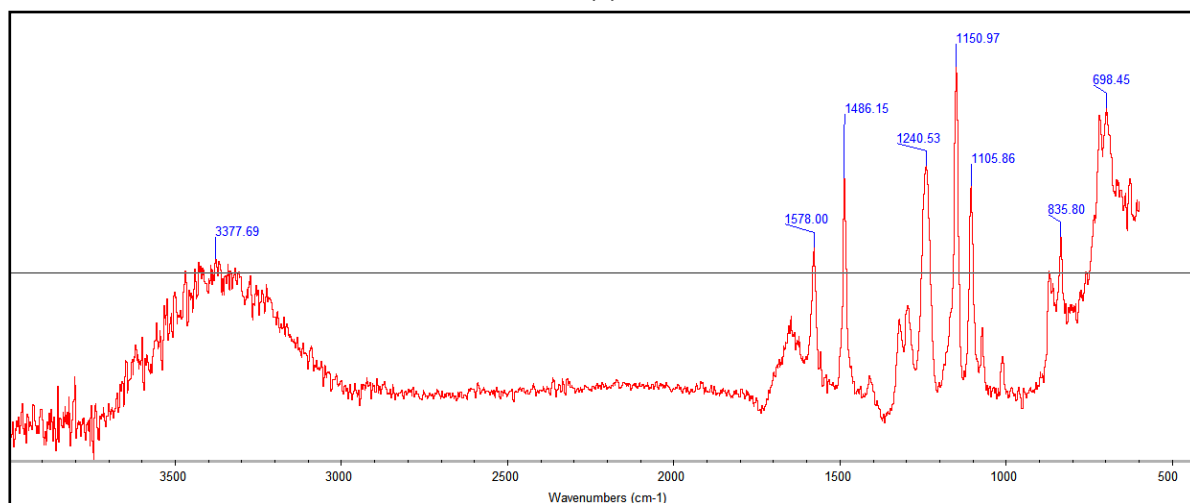


Fig. 1: Possible polymerization reaction between TEOA and TMC to form (A) totally cross-linked polymer chain, (B) polymer chain with pendant -COOH and (C) polymer chain with pendant -CH₂CH₂OH (Tang et al. 2008)

The results of the humic acid removal are presented in Figure 5 at 400 kPa. On the other hand, the result of the humic acid rejection of the membrane demonstrates a lower rejection of the humic acid for membrane modified at reaction time less than 6 min. However, the humic acid rejection increases slightly for membrane modified at longer reaction time (10 min and 15 min). The same trend was also observed by Tang et al (2008). When study the rejection of MgSO₄ solution. It is well known that the interfacial polymerization is diffusion-controlled and exists in a self-limiting phenomenon. Thus, the reaction time gives high impact to determine the extent of reaction. The top skin layer thickness of the composite membrane increases with increasing polymerization time. Top layer thickness will



(a)



(b)

Fig. 2: FTIR analysis of the uncoated membrane which contain PES/NMP/PVP and (b) thin-film composite polyester membrane (6% w/v TEOA at 5 min reaction time)

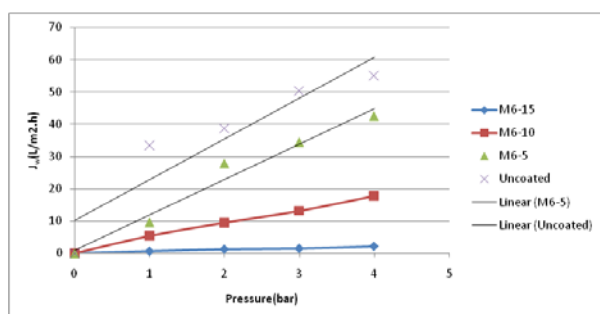


Fig. 3: Water flux of the uncoated and TFC membranes with different reaction times versus transmembrane pressure

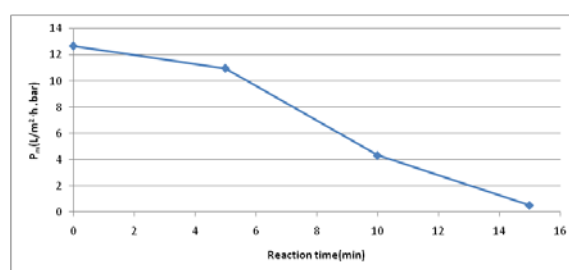


Fig. 4: Effect of different reaction time on membrane permeability

stop growing when the thickness of the thin layer is enough to prevent the monomer diffusing from one phase into the other

phase. As a result, the extent of cross-linking is low and the permeability of the membrane is high in the short reaction time.

However, the poor morphology of the membrane surface layer will be improved with the increase of reaction time and the membrane will gradually become integrated. Thus, the humic acid rejection increases slightly although the top layer thickness stops growing.

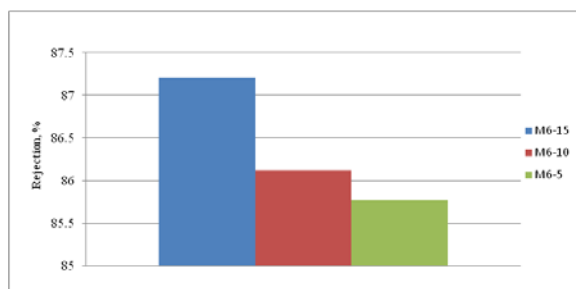


Fig. 5: Percentage of rejection to humic acid solution at 400kPa at pH 10

CONCLUSION

As water demand increases, environment and safety regulations are becoming stricter and a greater research efforts have been put into the improvement of membrane processes. Effective removal of such humic substances with membranes is a significant challenge in the water industry by controlling the reaction time of interfacial polymerization membrane. Interfacial polymerization method for producing TFC nanofiltration (NF) membranes has become an attractive alternative to conventional treatment for the removal of humic substances.

REFERENCES

Abu Seman M.N., Khayet M., Hilal N. (2010) .Nanofiltration thin-film composite polyester polyethersulfone -based membranes prepared by

interfacial polymerization. *Journal of Membrane Science* 348 109–116.

Ahmad A.L., Ooi B.S. (2005). Properties–performance of thin film composites membrane: study on trimesoyl chloride content and polymerization time. *Journal of Membrane Science* 255 67–77.

Alborzfar, M., Jonsson, G., & Grøn, C. (1998). Removal of natural organic matter from two types of humic ground waters by nanofiltration . *Water Research*, 32(10) , 2983-2994 .Doi : 10.1016 /S0043-1354(98)00063

Beverly S. Rubin. (2011) .Bisphenol A: An endocrine disruptor with widespread exposure and multiple effects, *Journal of Steroid Biochemistry & Molecular Biology* 127 27– 34

Jayarani M.M., Kulkarni S.S. (2000). Thin-film composite poly(esteramide) -based membranes, *Desalination* 130 17–30.

Vandenberg L.N., Hauser R., Marcus M., Olea N., Welshons W.V. (2007). Human exposure to bisphenol A (BPA), *Reprod. Toxicol.* 24 139–177.

Mamba B.B., Krause R.W., Malefetse R.W., Mhlanga S.D., Sithole S.P., Salipira K.L. and Nxumalo E.N. (2007).Removal of geosmin and 2-methylisoborneol (2-MIB) in water from Zuikerbosch Treatment Plant (Rand Water) using β -cyclodextrin polyurethanes. *Water SA* 33 (2) 223-227.

Mohammad A.W., Hilal N., Abu Seman M.N. (2003).A study on producing composite nanofiltration membranes with optimized properties, *Desalination* 158, 73–78.

Siddiqui M., Amy G.L., Ryan J., Odem W.

- (2000). Membranes for the control of natural organic matter from surface water, *Water Res.* 34 (13) 3355-3370
- Silverstein, R.M.; Bassler, G.C.; and Morrill, T.C. (1981). *Spectrometric Identification of Organic Compounds*. 4th ed. New York: John Wiley and Sons. QD272.S6S5
- Tang B., Huo Z., Wu P., (2008). Study on a novel polyester composite nanofiltration membrane by interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC) I . Preparation, characterization and nanofiltration properties test of membrane, *J. Membr. Sci.* 32
- Welshons W.V., Nagel S.C., vom Saal F.S., (2006). Large effects from small exposures. III. Endocrine mechanisms mediating effects of bisphenol A at levels of human exposure, *Endocrinology* 147 S56-S69.
- Wuilloud D.E. J.C., Wuilloud R.G., Sadi B.B. and Caruso J.A. (2003) . Trace humic and fulvic acid determination in natural water by cloud point extraction /pre-concentration using non-ionic and cationic surfactants with FI-UV detection. *The Analyst* 128 (5) 453-458.
-