

Performance of Cellulose Acetate – Polyethersulfone Blend Membrane Prepared using Microwave Heating for Palm Oil Mill Effluent Treatment

Ani Idris*, Iqbal Ahmed, Ho Wan Jye

*Department of Bioprocess Engineering
Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia, 81310 Skudai, Johor
Tel: +607-5535603, Fax: 607-5581463, Email: ani@fkkksa.utm.my

Abstract

The objective of this research is to investigate the performance of blend cellulose acetate (CA) - polyethersulfone (PES) membranes prepared using microwave heating (MWH) technique and then compare it with blend CA-PES membranes prepared using conventional heating (CH) method using bovine serum albumin solution. The superior membranes were then used in the treatment of palm oil mill effluent (POME). Various blends of CA-PES have been blended with PES in the range of 1-5 wt %. This distinctive series of dope formulations of blend CA/PES and pure CA was prepared using N, N-dimethylformamide (DMF) as solvent. The dope solution was prepared by MW heating for five minutes at a high pulse and the membranes were prepared by phase inversion method. The performances of these membranes were evaluated in terms of pure water and permeate flux, percentage removal of total suspended solids (TSS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Results indicate blend membranes prepared using the microwave technique is far more superior compared to that prepared using CH. Blend membranes with 19 % CA, 1-3 % PES and 80 % of DMF solvent were discovered to be the best membrane formulation.

Keywords

Blend membrane, cellulose acetate, microwave, polyethersulfone, POME

INTRODUCTION

Ultrafiltration membranes are usually anisotropic structures made by the Loeb-Sourirajan process. They have a finely porous surface layer or skin supported on a much more open microporous substrate. Ultrafiltration uses a finely porous membrane to separate water and microsolutes from macromolecules and colloids (Baker *et al.*, 2004). Many commercial polymeric membrane materials, such as polysulfone (PS), polyethersulfone (PES), polyvinylidene difluoride (PVDF), polypropylene (PP) and nylon have good chemical, thermal and mechanical stability. Compared with these mentioned materials, cellulose and its derivatives are hydrophilic and have reactive hydroxyl groups (Kesting *et al.*, 1993). Along with the ongoing search for new materials, modifications of existing polymers by blending have shown new directions in producing economical tailored materials so as to have desirable properties. The development of new types of materials provides great potential for application in various fields (Malik *et al.*, 1992). In recent years, the blend polymer membranes have been an attractive field and several blend membranes have been studied, manufactured and used (Bikson *et al.*, 1994; Chiou *et al.*, 1994; Wang *et al.*, 1996; Kaifen *et al.*, 1992; Yin *et al.*, 1997). Ideally, two or more polymers may be blended together to form products that show desirable combinations of properties. But this ideality is seldom attained due to some inherent and fundamental problems. Most of the polymer pairs are not thermodynamically miscible and so exist in two different phases in the polymer blend. Tomohiro *et al.* (1994) however has produced thermodynamically stable aromatic polysulfone and cellulose blends in a polar organic solvent such as N, N-dimethylformamide.

Dope solution preparation methods for the dissolution of polymer solids or powder samples for membranes in the laboratory scale are usually carried out in reaction vessels, typically 200 to 1000 ml. This mixture is heated for long period of time using a hot plate, heating mantle or oven. These conventional heating techniques are slow and time-consuming, and sometimes can lead to overheating and decomposition of the polymer and solution. Heating is stopped when the analyst decides that the dissolution of the sample is sufficiently complete. This type of reaction vessel digestion has many drawbacks, which include the use of large volumes (and multiple additions) of materials, a large potential for contamination of the sample by materials and laboratory environment, and the exposure of the analyst and the laboratory to corrosive fumes (Robert *et al.*, 2003). To overcome these problems, microwaves have been employed in organic chemistry to reduce the reaction times from hours to minutes, to increase yields and selectivity (Stuerga *et al.*, 1993). Swatloski *et al.* (2004) have dissolved cellulose in ionic liquid under microwave heat within 15 seconds heat pulse whilst Wang *et al.* (2002) have used microwave heating to assist the dissolution of high molecular weight β -glucan in water without polymer degradation in 4-10 minutes. Recently, Ani *et al.* (2006) have prepared organic membranes from dope solutions prepared using the microwave technique and revealed that the membranes produced are far more superior in terms of flux rate compared to those prepared using the CH method.

Although microwave technology has been used to accelerate the organic reactions in organic chemistry since 1970s, it has never been used for the preparation of organic membranes. Besides Tomohiro *et al.* (1994) who has produced the first CA/PSf blend semipermeable membrane, Sivakumar *et al.* (2006) has also produced CA/PES blend with additives PVP and PEG. In most of these work, the blend membrane dope solution were prepared using the CH methods which takes approximately 4 hours. Thus in this study an attempt is made to produce blend membranes using the MWH technique and its performance is compared with the membranes produced using CH method.

The membranes produced were initially tested for BSA and then used for POME treatment since the palm oil industry is one of the major agro-industries in Malaysia and considerable quantities of wastewater are discharged. The performances of the membranes produced were evaluated in terms of flux and percentage rejection of total suspended solids, COD, BOD and turbidity.

MATERIALS AND METHODS

The PES used was supplied by BASF. The solvent N, N-dimethylformamide (DMF) was purchased from Labscan Asia Co. Ltd, and used without further purification. Bovine serum albumin (BSA) with molecular weight of 69000 Daltons was supplied by Merck and used as the feed solution. CA with 39.8 acetyl content from Acros organic was used. For UF experiments, samples of palm oil mill effluent (POME) at 80 °C were collected from the Felda Bukit Besar Kulai, Johor. These samples were allowed to cool to room temperature and left to sediment by filtration process. Portions of the suspension were withdrawn and analyzed.

Dope solution preparation

The 300 ml dope solutions that consist of 1 % - 5 % PES and 80% DMF shown in Table 1 were prepared by two different methods described below:

a) Microwave heating (MW) method: In this study, Sharp domestic microwave oven model R-4A53 with the following specifications were used. It has a rated power out put of 850 watts (240V~50 Hz), operation frequency of 2450 MHz. A 500 ml Schott Duran is used as the sample reaction vessel at atmospheric pressure. Mercury thermometer was used manually to control the temperature at every 20 sec. The temperature of the dope solution was kept at 85-95 °C. Heating time by microwave was 5 minutes.

b) Conventional electro heating (CH) method: In the conventional electro heating, the polymer dissolution process is carried out in a 1 liter 3 necked round bottomed flask with stirrer and condensers. The electro thermal heater used is (230V~50/60 Hz, 300 Watts) under the brand name Barnstead/electro thermal. The dope temperature is kept constant at 90 °C by stirring and the dissolution of polymer takes 6 hrs.

Membrane casting

In this study, the membranes are prepared by phase inversion method. The dope solution thus obtained was spread over a smooth glass plate with the help of a casting knife. The thickness of the membranes was controlled by varying the thickness of adhesive tapes at the sides of the glass plate.

Table 1 Dope solution compositions.

Dope Solution	Composition (wt. %)		
	CA	PES	DMF
1	20	0	80
2	19	1	80
3	18	2	80
4	17	3	80
5	16	4	80
6	15	5	80

The glass plate was kept in an environment of controlled temperature and humidity during membrane casting. No deliberate solvent evaporation period was allowed. The glass plate was subsequently immersed in a water bath.

Viscosity Measurements

The viscosities η (cps) of blend dope solutions produced are measured using Brookfield rheometer (model DV-III ultra, USA) and CC 31 rotating-cylinder sensor system at 30°C temperature, controlled by water bath. The viscosities for these dope solutions were obtained at 5 and 10 rpm.

Determination of permeation flux and solutes rejection

Flux and rejection rates of membranes were measured using an ultrafiltration cross flow ultrafiltration unit. At first, pure water or the feed solution was pumped to the flat sheet module by a pump at 3.5 bars, and was circulated through the module for 1 h (pressure drop = 0.5 psig). The % rejection of the membranes was tested with 1000 ppm BSA solution. The absorbance of original liquids and permeated liquids was measured using a spectrophotometer while the flux and rejection were calculated from following equations:

$$J = \frac{Q}{\Delta T \times A} \quad (1)$$

where J is the permeation flux of membrane for PEG solution ($\text{L m}^{-2} \text{h}^{-1}$) or pure water and Q is the volumetric flow rate of permeate solution.

Solute rejection of membranes was evaluated with BSA solutions of molecular weight 69 kD at 3.5 bar. The concentration of BSA solution used is 1000ppm. The concentration of the feed and permeate solution were determined by the method described else where (Sabde *et al.*, 1997).

The membrane rejection (R) is defined as

$$R = 1 - \frac{C_p}{C_f} \times 100 \% (2)$$

where C_f and C_p are the BSA concentrations in the feed solution and permeate solution, respectively. The concentration of BSA was determined based on absorbency in a UV-spectrophotometer at a wavelength of 535 nm.

Palm Oil Mill Effluent (POME)

The raw POME sample was treated via filtration process to remove the suspended matter. The pH of POME before the treatment was 8 and after the pretreatment process was 6.5 and density was 1.25 gm/cm^3 at 30°C . Membrane performances were investigated by ultrafiltration experiments using the experimental procedure described earlier with BSA samples. The permeated POME was also analyzed in terms of turbidity, TSS, BOD and COD for its separation performance as described in the following section.

(a) Chemical Oxygen Demand (COD) Test: 2 ml sample was put into contact with the oxidizing acid solution that was then held at 148°C for 2h. After cooling, the sample was then analyzed in the HACH DR/2000 and DO readings were taken at 435 nm wavelengths. The color of the sample varied from orange to dark green indicating COD strength in the range of 0 – 15,000 mg/L.

(b) Biochemical Oxygen Demand (BOD) Test: Samples may have to be diluted in order for the dissolved oxygen (DO) to be detected by the meter. Once all the bottles have been filled, in a 500 ml BOD flask the initial DO's of each solution is determined using dissolved oxygen meter (model YSI 5402). Once recorded, the bottles are capped with ground glass stoppers to avoid excess bubbles. After five days of incubation at 4°C , the samples are ready to be analyzed. The samples are removed from the incubator and allowed to equilibrate to room temperature. Once the DO meter is calibrated, the samples are read starting with the blanks and ending with the actual samples. The final DO of each solution is recorded and the initial and final readings will be used to calculate the BOD.

(c) Turbidity and Total Suspended Solid Test: The turbidity of the samples was measured using HACH Ratio/Xr Turbidimeter which was calibrated. Total suspended solids were measured by inserting a glass microfiber filter disc with wrinkled side up in the filtration apparatus. Vacuum and wash disc with 50 mL of reagent-grade water is then applied. Suction is sustained to remove all traces of water. Next, the vacuum is then turned off. Sample is to be dried in an oven at 103 to 105°C for an hour. Next, the sample was then cooled down to room temperature before weighing. The cycle of vacuum, drying, cooling and weighing with 20 ml of sample is repeated. The total suspended solid is calculated according to equation 4.

$$\text{Total suspended solids mg/L} = \frac{(A - B) \times 1000}{v} \quad (3)$$

where A is weight of filter + dried residue, mg, B is weight of filter, mg and v is volume of sample used. The efficiency of the membrane fabricated is highly dependent upon the total removal of the component using the following equation:

$$\text{Total removal (\%)} = \left(\frac{\text{Initial Concentration} - \text{Final Concentration}}{\text{Initial Concentration}} \right) \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Viscosity Characterization

Table 2 exhibits the viscosities of both the blend polymer dope solutions prepared by MWH and CH technique at 5 and 10 rpm. These values were further plotted and depicted in Figure 2. In general it is observed that dope solutions prepared using MWH have much lower viscosities compared to those prepared by CH. This is attributed to the rapid dissolution of PES and CA in DMF within 2 minutes at high pulse. As the PES content increases, the viscosity of dope solutions prepared using CH increases until the PES content reaches 3 % wt and then it decreases slightly. However for dope solutions prepared using MWH, the presence of 1 % wt PES decreases the viscosity of solution to

Table 2 Viscosities of casting solutions with two different techniques at 30 °C

PES wt %	Viscosity of Dope Solution by MW (cps)		Viscosity Dope Solution by TM (cps)	
	η_{MWH} at 5 rpm	η_{MWH} at 10 rpm	H_{CH} at 5rpm	H_{CH} at 10 rpm
0%	2118	1912	2235	2107
1%	1074	1017	2289	2289
2%	2277	2277	2489	2489
3%	2340	2340	2453	2453
4%	1842	1842	1950	1950
5%	1899	1899	2184	2184

as low as 1074 cps. Beyond 1% wt of PES the viscosity begins to increase but their viscosities are much lower than the viscosities of the dope solutions prepared using CH. It is believed that at 1 % wt PES, the hydrophobic and hydrophilic effect from both polymers is balanced but this balance effect is more mature in MWH dope solutions. Using the MWH technique blend dope solutions with PES content as high as 5 % wt can be prepared easily in a very short time and the low viscosity enables easy handling in the casting and spinning of membranes.

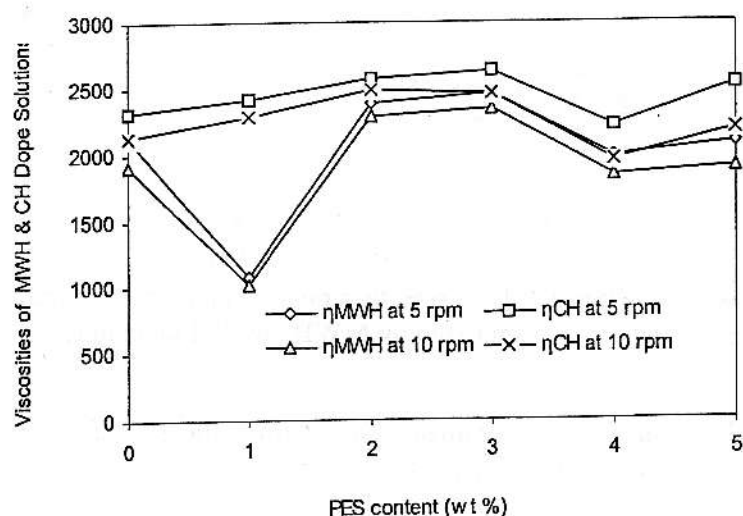


Figure 1 Viscosities of dope solutions prepared using both the MWH and CH techniques.

Performance of Blend Membranes using BSA as feed solution

The performance of the blend membranes produced by both MWH and CH were initially tested using BSA solutions. The pure water permeation and BSA rejection rate results were depicted in Figure 2 and 3 respectively. It is observed in Figure 2, that the membranes produced from CH dope solutions exhibited good performance in terms of PWF compared to MWH. The highest PWP is achieved when the PES content reaches 5% using both techniques. The BSA rejection rate results of both techniques were depicted in Figure 3. The performance of the blend membranes in terms of BSA rejection produced by MWH exhibited higher rejection of BSA compared to CH. However the rejection rates of higher composition of PES in CA blend membrane is the lowest compared to the other membranes containing less amounts of PES. Apparently membranes produced by MWH with PES content of 1 to 3% exhibits highest rejection rate with molecular cut off (MWCO) at 90% of approximately 69 kDa (BSA). Compared to membranes prepared by CH these membranes prepared by MWH are not only superior in terms of rejection rates but their flux rates are as reasonably high as those prepared using CH.

Performance of Blend Membranes in POME

Since the performance of membranes prepared using the MWH technique are far more superior in terms of BSA separation, they are then used for the treatment of POME. The POME was initially filtered as a pretreatment step for the samples before undergoing cross flow ultrafiltration process. Pretreatment steps were performed so as to eliminate a large portion of solid fraction in the samples. It is observed that the raw POME sample has high concentration of waste. This study abides by the same trend of pretreatment via centrifugation, a process which is used to remove organic pollutant loads before ultrafiltration experiments. The results indicates in Table 3 that there is a reduction of 186 mg/L or 41.24 % in BOD, 1294 mg/L or 41.0 % in COD, 11400 mg/L or 95.12 % of suspended solids and 6826 NTU or 95.12 % turbidity. This implies that some of the organic and suspended solids content has been removed by filtration before ultrafiltration process. The results in Figure 4

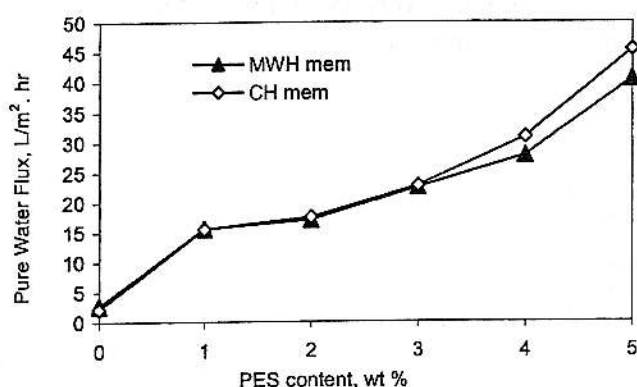


Figure 2: Pure water flux of blend membranes prepared by MWH and CH technique

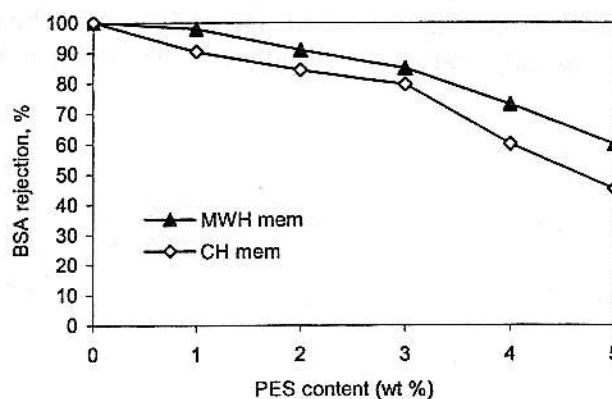


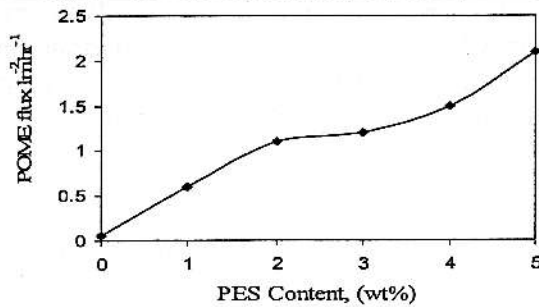
Figure 3: BSA rejection rates of blend membranes prepared by MWH and CH technique

revealed that membrane with 5% PES exhibits the highest permeate flux during the POME ultrafiltration process, followed by membranes with 4, 3, 2, 1 and 0% PES.

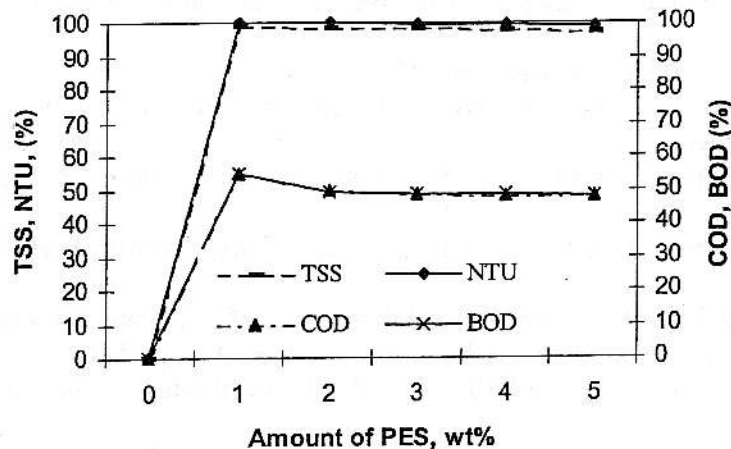
Results indicated presence of PES in dope solution improved the flux rate of membranes. Apparently the presence of PES acts as a pore former in the dope solution where permeation rates are observed to increase. However the amounts should be limited to about 3 % PES because of its separation performance as shown in Figure 5.

Table 3 The efficiency of pretreatment

	Raw POME	POME After Filtration	Reduction	Percentage of Removal, %
TSS (mg/L)	11985	585	11400	95.12 %
Turbidity (NTU)	7140	314	6826	95.602 %
COD (mg/L)	3156	1862	1294	41.0 %
BOD (mg/L)	451.00	265.00	186.00	41.24 %

**Figure 4** Flux during POME separation

Results tabulated in Figure 5 shows that the separation performance of POME in terms of total suspended solids (TSS), turbidity (NTU), COD and BOD for the membranes tested. The blended membranes fabricated are capable of reducing POME turbidity to 95.602 % and its total suspended solid by 95.12 %. This directly implies that some content of suspended solids has been removed prior to membrane treatment stage. The results also proved that blended CA-PES membranes exhibit excellent performance in POME waste water treatment. Membrane 2 with 1% PES shows the best result with 99.972 % of turbidity removal and 98.71 % in removal of TSS. This is followed by membrane 3, membrane 4, membrane 5 and membrane 6 respectively. COD is an indication of the overall oxygen load that a wastewater will impose on an effluent stream. COD is equal to the amount of dissolved oxygen that a sample will absorb from a hot acidic solution containing potassium dichromate and mercuric ions. The performance of COD shows the reduction by 54.75 % for the membrane 2, 49.37 % for membrane 3, 48.73 % for membrane 5 and 47.72 % for membrane 6. The BOD of wastewater expresses the amount of oxygen used by biodegradable organic substances. The amount and presence of PES content in the CA membranes plays an important role in reducing the BOD percentage to 54.55 %, 54.77 %, 49.38 %, 48.75 % and 47.74 % for membrane 2, 3, 4, 5 and 6 respectively. The BOD reduction shows a similar trend to the COD reduction as illustrated in Figure 5.

**Figure 5** Percentage of removal in terms of total suspended solid (TSS), turbidity (NTU), COD and BOD for the membranes tested

CONCLUSION

In summary CA/PES ultrafiltration blend membranes produced from dope solutions prepared using the microwave technique are far more superior in terms of rejection rate compared to those prepared using the conventional electro heating method. The performances of the PES ultrafiltration membranes revealed that membranes with the formulation, 1% -3 % exhibited the best rejection rates of and reasonably high flux. The percentages of removal for turbidity, TSS, COD and BOD were 99.975 %, 99.12 %, 54.75 % and 54.77 % respectively. The MWH technique could work in favor to thermodynamically enhance the blending process, thus decrease the viscosity of the CA/PES blend dope solution, which is very favorable for good blending to both polymers and also ease handling problems. Apparently microwaves result in rapid heat transfer which accelerates the polymer particles vibration thus speeds up the dissolution of the polymer in the solvent. Thus this novel microwave method has proved to be a very rapid and economical process and has the potential to bring membrane technology to new heights.

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