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The Development of a New Polymer Membrane : PSf/PVDF blended Membrane

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ABSTRACT

This article reports Polysulfone (PSf) membrane modification efforts by blending method using polymers Polyvinylidene fluoride (PVDF) superimposed on polyesther. This study aims to obtain asymmetry structure in cross section of PSf-PVDF blended membrane formed by applying a combination of the use of varied immersion temperature and frequency of non-solvent uses in the membrane preparation process. Polysulfone-Polyvinylidene fluoride blended membrane in this study was prepared by phase inversion method with immersion precipitation techniques. The casting solution of PSf-PVDF blended membrane made of PSf and PVDF polymer as main components, N-methyl pyrrolidinone (NMP) as a solvent and ammonium chloride (NH_4Cl) as an additive. For inducing phase inversion on the casting solution, used H_2O as non-solvent. Morphology of the PSf-PVDF blended membrane forms have been analyzed by Scanning Electron Microscopy (SEM) with a power of 20 kV; the results show the asymmetry structure on the cross-section morphology of all types of PSf-PVDF blended membrane which prepared. Formation of asymmetric structure in PSf-PVDF blended membrane is able to increase the permeability and selectivity of PSf-PVDF blended membranes against batik dyes, such as naphthol and indigosol types, which hypothetically caused by macrovoid creation on the membrane during the phase inversion process.

Keywords : membrane, PSf, PVDF, assymetric structure.

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INTRODUCTION

One of the polymer materials widely used in the form of membranes for textile wastewater treatment is polysulfone [1]. Polysulfone known for its high thermal and chemical resistance, and also well mechanic [2]. Polysulfone has limitations on the symmetry's structure, range of pore size and porosity that led to reduce the use of these membranes [3-4]. These limitations are caused by the symmetry structure which generally has high fouling potential due to complexity of the pore structure [4]. The fouling occurance on membrane has been shorten the functioned duration and led to increasing operating costs of membrane. Therefore, membrane fouling was concluded as one of causes for limiting the use of it in industry. Research and development of new membrane materials are the most effective way to suppress the membrane fouling. Potential membrane material must be commercially available, having thermal stability, good chemical resistance which is able to against the corrosion caused by acids, bases and bacteria, as well as having the characteristics of the formation and good mechanical strength [5-8].

Currently, polyvinylidene fluoride (PVDF) is one of promising polymeric membrane materials, which has received considerable attentions, due to its chemical durability which is excellent in resisting the corrosive material, such as acids, bases, and oxides, high flexibility, as well as having good characteristics on formation and permeability (9-15). Thus, PSF needs to be modified by PVDF, to obtain characteristics of the membrane that needed.

Many researchs have been conducted to improve membrane performance, such as physical blending, chemical grafting, and modifying surface [16-18]. Among those three methods, polymer blending method has advantages in the easiness of preparation process by using a phase inversion [18].

The PSf-PVDF blended membrane in this paper areprepared by immersion precipitation process. In this process, a polymer solution was casted on the solid support (substrate) and then immersed into a coagulation bath containing non solvent to induce a series of liquid-liquid and/or liquid-liquid phase separations [16-21]. In the drying procedure, the liquid phase is separated and produce dense porous membrane [21].

This study aims to prepare porous PSf-PVDF blended membranes in the type of sheet, with good morphological control and high permeability. Specifically, this research is directed to determine the effect of immersion temperature and the frequency of non-solvent uses (no-solvent purity) to membrane morphology, permeability and mechanical strength. At the same time, it has also investigated the rejection of the membranes against dyes.

EXPERIMENTAL

Materials

The materials used in this research include: (a) the membrane materials: PSf (Pellet Mw 35,000 by LS, Aldrich), PVDF (Powder Mw 534,000, Aldrich), N-methyl-2-pyrrolidinone (NMP) (biotech grade, ≥99,7%, Sigma Aldrich), Ammonium chloride (NH4Cl (≥99,5%, Riedel de Haen) and pure water; and (b) material to examine the permeability and selectivity of membranes are 7 (seven) types of dye batik including pink indigosol, blue indigosol, yellow indigosol, purple indigosol, red naphthol, yellow naphthol, blue naphthol (obtained from SMEs Batik Namiroh, Sidoarjo, Indonesia) and distilled water.

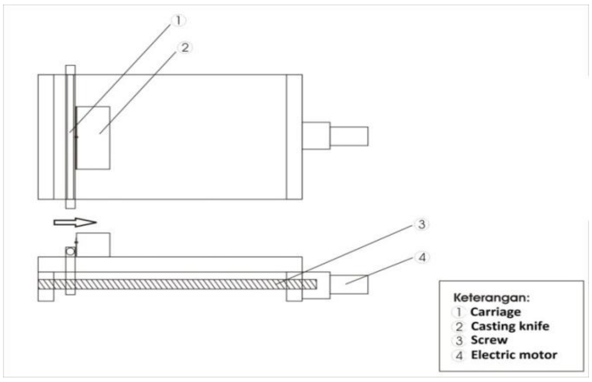
Casting solution preparation

The PSf-PVDF blended membrane with blending solution composition (PVDF/PSF/NMP/NH_4Cl) (%w/w) 12/2/84/2 prepared as followed. Two gram of PSf and 2 g of NH_4Cl dissolved in 84 g of NMP solvent. Then, to ensure the formation of a homogeneous blending solution, the solution has stirred with a magnetic stirrer for 105 minutes at 60 °C, then add 12 g of PVDF and continued the stirring process up to 15 minutes.

The homogeneous blending solution then casted on the polyester supporting layer by using casting knife with a thickness of 0.8 mm. In order to remove air bubbles which trapped in the blending solution, the solution has settled for 5 minutes. The dense PSf-PVDF blended membrane are obtained after immersing the blending solution into coagulation bath that containing non solvent 100% H_2O in immersion temperature 40

°C. Membranes were transferred from the glass mold and immersed in water overnight to remove the remnants of solvents and porogen were left. The last process was drying the membrane in the open air for 24 hours.

By changing the immersion temperature and non solvent frequency uses (non solvent purity), membrane with various morphology and transport properties could be obtained. Figure 1 illustrates the knife casting use in the casting process of the membrane.



Gambar 1. Utilizing casting knife on the casting process of PSf-PVDF blended membrane with polyesther supporting layer [22]

Membrane characterization

Determining the success of PSf-PVDF blending, chemical groups are analyzed by using Nicolet IS10 Thermo Fourier Transform Infra Red (FTIR). In addition to knowing the success of asymmetry structural forming on the PSf-PVDF blended membrane, physical characterization was carried out by using a Zeiss EVO MA10 scanning electron microscope (SEM) on the surface and cross section of the membrane.

Samples for cross sections morphological analysis using SEM were prepared by cryogenic breaking of fresh wet films using liquid nitrogen and then coated with a thin gold layer. While mechanical strength was measured with Shimadzu AG-10TE autograph.

Analysis of the membrane performance

To measuring the transport characteristics of the membrane to water, a membrane reactor (homemade) with a capacity of 1 L and the effective membrane area of 19.64 cm^2 was used. The pressure required to flow test the membrane is obtained from the compressor. Water flux values are calculated from measurements of permeate per unit volume at a pressure of 1 atm and a temperature of 25 °C. Before the flow test, the membrane was conditioned by flowing water on the membrane using a pressure of 1 atm.

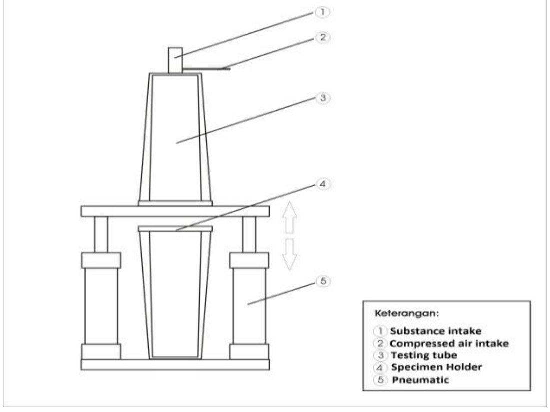


Figure 2. The dead end membrane reactor [22]

Rejection of solute was measured at 1 atm pressure using the same equipment and used the feed solution such as purple indigosol, yellow indigosol, pink indigosol, blue indigosol, red naphthol, yellow naphthol, and blue naphthol, which were prepared by using 1 L pure water with solute concentration is equal to 5 mg/L. The solute concentration resulting from the flow test, measured using Shimadzu UV-1700 UV-Visible spectrophotometer. Rejection was calculated using the following equation:

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

Where C_p is the concentration of permeate and C_f is the concentration of feed.

Mechanical strength and elongation

The mechanical strength and elongation of the blended membrane were measured by using autograph (AG-10TE, Shimadzu Co., Japan). The membrane is placed vertically between two part of clamps within 50 mm distance. Furthermore, the membranes is pulled with a constant elongation rate of 50 mm/min until it was broken [12]. The average of the three membranes was taken as the mean mechanical strength and elongation for each type of blended membranes.

RESULT AND DISCUSSION

Membrane charaterization

The infra red spectra of the **PSf-PVDF** blended membrane shown in Figs. 3. From the result shown in Figs. 3, it is evident that the **PSf-PVDF** blended membrane was formed. Chemical characterization of the membranes is performed to determine the success of the blending process done by comparing the IR spectra of **PSf-PVDF** blended membrane with IR spectra reference (IR spectra of PVDF and PSf membrane). Results of the infra red analysis of a blended **PSf-PVDF** membrane with FTIR are shown in figure 3.

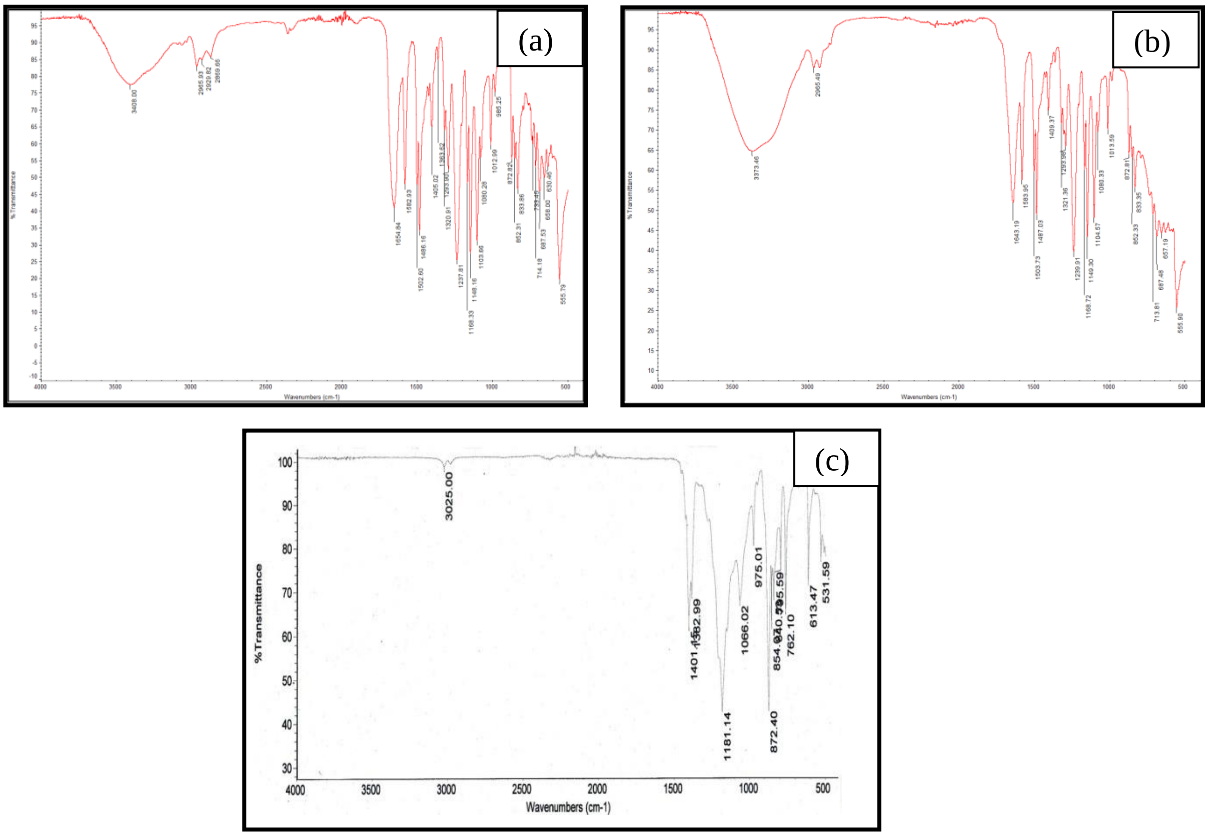


Figure 3. The infrared (IR) spectra: (a) PVDF membrane; (b) PSf membrane; and (c) PSf-PVDF blended membrane

Based on data from the infrared spectra of PVDF membrane (a) obtained, it was detected the PVDF molecule character, which are : (a) peak at wavenumber 3025 cm^{-1} indicating the presence of aliphatic C-H; (b) peak at the wavenumber 1066.02 to 1181.14 cm^{-1} indicating the presence of C-F. Meanwhile, based on infrared spectra data of polysulfone membrane (b), it was detected the distinctive character of the polysulfone molecule: (a) peak at wavenumber 3408 cm^{-1} indicating the presence of alcohol functional group O-H; (b) peak at the wavenumber 2965.93 cm^{-1}; 2929.82 cm^{-1}; and 2869.66 cm^{-1} indicating the presence of a (C-H) functional group of alkane; (c) peak at the wavenumber 1654.84 cm^{-1} indicating the presence of a C = C functional group of alkenes; (d) the peak at wavenumber 1654.84 cm^{-1}; 1582.93 cm^{-1}; 1502.60 cm^{-1} and 1486.16 cm^{-1} indicating the presence of a C = C functional group of aromatic; and (e) peak at the wavenumber 1148.16 cm^{-1} indicating the presence of a C-O functional group of ether.

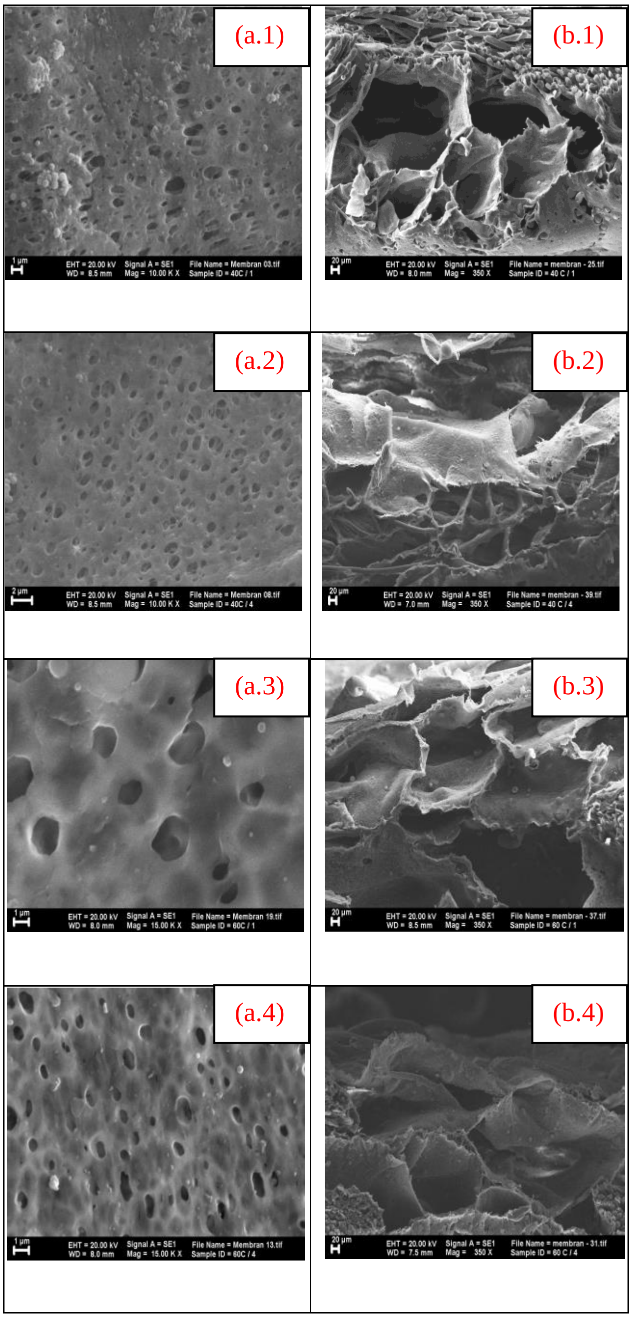


Figure 4. The surface (a) and cross section (b) morphology of PSf-PVDF blended membrane PVDF/PSf/NMP/NH_4Cl (%b/b) 12/2/84/2l; non solvent 100% H_2O : (1) immersion temperature 40 °C and frequency of non solvent use 1x; (2) immersion temperature 40 °C and frequency of non solvent 4x (magnification 15.000x); (3) immersion temperature 60 °C and frequency of non solvent use 1x; (4) immersion temperature 60 °C and frequency of non solvent 4x (magnification 15.000x)

Meanwhile, based on infrared spectra data of PVDF-PSF blended membrane resulting from the preparation process by stirring temperature 40 °C, PVDF and PSf molecule characters are detected: (a) peak at the wavenumber 3373.46 cm^{-1} indicating the presence of OH functional group of alcohol; (b) peak at the wavenumber 2965.49 cm^{-1} indicating the presence of C-H functional groups (aliphatic); (c) peak at the wavenumber 1643.19 cm^{-1} indicating the presence of a C = C functional group of alkenes; (d) the peak at wavenumber 1643.19 cm^{-1}, 1583.95 cm^{-1}, 1503.73 cm^{-1}, and 1487.03 cm^{-1} indicating the presence of a C = C functional group (aromatic); (e) peak at the wavenumber 1149.30 cm^{-1} indicating the presence of CO functional group of ether; and (f) the peak at wavenumber 1013.59 cm^{-1}, 1080 cm^{-1}, and 1104.57 cm^{-1} indicating the presence of C-F functional groups.

The SEM photographs of the surface and cross sectional morphology of PSf-PVDF blended membranes are shown in Figs. 4. From the results shown in Figs. 4, it is evident that the PSf-PVDF blended membrane resulted from the preparation process using pure non solvent (not contaminated with NMP) seem to have asymmetric structure with a larger pore size than the membrane obtained from the preparation using non solvent with 4 times frequency of uses.

The condition due to NMP contamination in the non solvent H_2O has caused a delay in the process of liquid-liquid demixing as the result of solubility parameter differences that was created between the solvent and non-solvent (a mixture of solvent and non-solvent) increasingly smaller. Variations on time that required in phase separation and formation of PSf-PVDF blended membranes were strongly affected by the relative affinity between the solvent and polymers as well as thermodynamics disruption to chemical equilibria of the membranes casting solution, which is induced by the exchange process between the NMP molecules as a solvent with H_2O molecules as a non-solvent.

The relative affinity between the polymer and solvent can be determined by using the Hansen solubility parameters including polar component (δp), dispersion force component (δd), and the hydrogen bonding component component (δh). Because materials with solubility parameter values adjacent to each other will tend to dissolve, the the interaction between the polymer and solvent defined in equation 1, can be used to test the relative affinity of PVDF and PSF with NMP and also NH_4Cl with NMP:

$$\Delta\delta_{ps} = [(\delta_{ps} - \delta_{pp})^2 + (\delta_{ds} - \delta_{dp})^2 + (\delta_{hs} - \delta_{hp})^2]^{1/2} \qquad (2)$$

With the provisions of p dan s, each representing a polymer anda solvent [23-25]. Table 1 lists the solubility parameters of PVDF, PSf, NMP, H_2O and CH_3OH.

Table 1. The solubility parameters of the membrane materials [26-28]

	δ_d	δ_p	δ_h	δ_t
PVDF	16	14,3	23,9	32,12
PSf	19,7	8,3	8,3	22,93
NMP	18	12,3	7,2	22,9
H_2O	12,2	22,8	40,4	48,0
CH_3OH	11,6	13,0	24,0	29,7

$$\Delta H_m = V_m . [(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)]^2 . \emptyset_1 . \emptyset_2 \qquad (2)$$

Where, ΔHm = total heat of mixing; Vm = total molar volume of the mixture; ΔE_1= vaporization heat of component 1; ΔE_2 = vaporization heat of component 2; V_1 = molar volume of component 1; V_2 = molar volume of component 2; $\emptyset_1$= the volume fraction of component 1; $\emptyset_2$ = the volume fraction of component 2.

On the other hand, the increasing of immersion temperature in the preparation process of PSf-PVDF blended membrane turned out to produce membranes with smaller pore sizes. This is particularly evident in the surface and cross section morphology of PSf-PVDF blended membrane (figure 4). The increasing of immersion temperature automatically increases the thermodynamic disturbance in the reaction equilibria of casting solution, as a result of the increased heat of mixing (ΔH) when casting solution poured into the coagulation bath containing a non solvent. In Figure 4 clearly seems that the asymmetry structure has been formed in all kinds of PSf-PVDF blended membrane that produced.

However, the emergence of a significant differences in the PSf-PVDF blended membrane that produced by applying different immersion temperature was not apparent in immersion temperature of 40 °C and 60 °C with frequency of the non-solvent use 4 times. On this case, the use of membrane pore size data becomes an increasingly important, considering the results of the SAA analysis can shown pore diameter at the larger part of the membrane as compared to the membrane portion imaged by SEM instrument. In addition, analysis using the SEM instrument was strongly affected by the imaged part of the membranes, specially when formed symmetry structure. On the membrane with asymmetry structure, the top layer of the membrane (at the time of coagulation) will have pores with a greater diameter than the bottom layer of the membrane, so the imaging process on the same side of the membrane to be compared becomes very important.

Membrane Performance

The effect of immersion temperature and frequency of non solvent uses on permeablity and mechanical strength of PSf-PVDF blended membranes

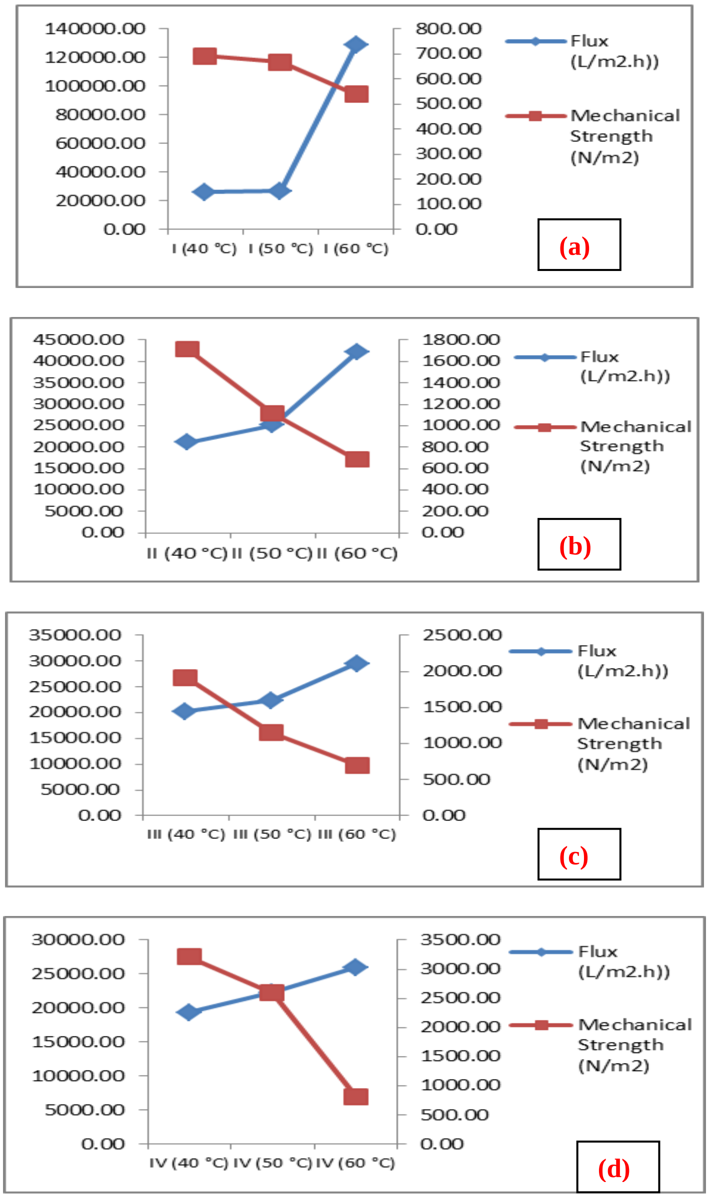


Figure 5. Effect of the immersion temperature and non solvent frequency uses on permeability and tensile strength PVDF/PSf blended membrane with non solvent frequency uses: (a) 1 times; (b) 2 times; (c) 3 times; and (d) 4 times

Fig. 5 was displaying of effect of the immersion temperature and frequency of non solvent uses on permeability and mechanical strength of PSf-PVDF blended membrane when the immersion temperature was 40 °C (a); 50 °C (b); and 60 °C (c), respectively.

Those four graphic in figure 5, all stated that the maximum flux can be achieved when the immersion temperature was 60 °C and frequency of non solvent uses was 1 time. However, when the immersion temperature was changed from 60 °C to 40 °C with frequency of non solvent uses 2 times, the mechanical strength increased much equal with flux, so the proper immersion temperature and frequency of non solvent uses should be 40 °C and 2 times.

Table 2: The flux and rejection of PVDF/PSf blended membrane (immersion temperature : 40 °C; frequency of non solvent uses : 2 times) against different dyes

Solute (5 mg/l)	Flux ($L/m^2.h$)	Rejection (%)
Purple Indigosol	22302.67	72.66
Pink Indigosol	14154.28	11.50
Blue Indigosol	24524.00	49.85
Yellow Indigosol	22329.82	33.39
Red Naphtol	2813.49	63.39
Yellow Naphtol	3602.15	47.28
Blue Naphtol	5991.82	14.57

CONCLUTION AND REMARKS

On this article, PSf-PVDF blended membrane has prepared by phase inversion method. For membrane preparation process, has been done variation on immersion temperature and the frequency of non-solvent uses (purity of non-solvent) that used, so it can be obtained varying morphology, mechanical strength and permeability of the membrane. The morphology, mechanical strength and permeability of the membrane greatly influenced by immersion temperature and frequency of non-solvent uses (purity of non-solvent) that used for the membrane preparation. The main conclusions are as follows.

- The higher immersion temperature and more pure non solvent used in the membrane preparation process, will further enhance the membrane pore size and permeability to water and dye feed solutions, but on the other hand, will also reduce the mechanical strength of PSf-PVDF blended membrane.
- The PSf-PVDF blended membrane has rejection ability, each are 72.66% for purple indigosol; 11.50% for pink indigosol; 33.39% for yellow indigosol; 49.85% for blue indigosol; 63.39% for red naphtol; 47.28% for yellow naphtol; and 14.57% for blue naphtol.

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