**Physicochemical properties of PSF/SiO<sub>2</sub>-NH<sub>2</sub> composite membranes incorporated by polymeric additives** 

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### ABSTRACT

This research project aims to study the effects of PVP and PEG on the morphological structure, hydrophilicity and mechanical properties of PSF/SiO<sub>2</sub>-NH<sub>2</sub> nanoporous composite membranes. To investigate the physical and chemical properties as mentioned above, pure PSF and composite of PSF/SiO<sub>2</sub>-NH<sub>2</sub> membranes with and without the addition of PVP and PEG are fabricated by phase inversion method. Alteration of characteristics of synthesized membrane samples are evaluated by different analytical techniques. Hydrophilicity of membrane surfaces is analyzed through the measurement of water contact angle (WCA) while morphological structure and pore size as well as physical structure are evaluated through the SEM micrographs. Variation of hydrophilic functional group is analyzed by FTIR technique. Results showed that PVP and PEG clearly affect morphological and porous structures of composite membranes. Porous structure have changed from sponge-like structure with macrovoids to finger-like structure. Macrovoids disappeared when PVP and PEG were incorporated into the matrix of PSF/SiO<sub>2</sub>-NH<sub>2</sub> composite membranes. Importantly, nano-size pore appeared on the top surface of PSF/SiO<sub>2</sub>-NH<sub>2</sub> membranes incorporated with PVP and PEG also influence the hydrophilic properties of membrane samples. This effect is confirmed by increasing of hydrophilic group on the composite membrane surfaces and decreasing of WCA.

**Keywords:** Composite membranes, PSF/SiO<sub>2</sub>-NH<sub>2</sub>, morphological structure, hydrophilic properties, PVP and PEG

## Materials and Experimental method

N-Methyl-2-pyrrolidone (NMP,  $C_5H_9NO$ , 99.0% purity,  $M_W$ :99.13 g/mol), polyvinylpyrrolidone (PVP360, average molecular weight of 360,000) and 3-Aminopropyl triethoxysilane (APTES) were supplied by Sigma-Aldrich (USA). Polyethylene glycol (PEG1000), Tetraethylorthosilicate (TEOS,  $M_W$ : 208.33 g/mol) and Cetyltrimethylammonium bromide (CTAB, >98.0 % purity, MW:364.45 g/mol) were supplied by Merck, Thailand. Pellet PSF materials (Udel P-3500 LCD MB) were supported by Solvay, China. Ethanol (EtOH, AR. Grade) and cyclohexane (CHX,  $C_6H12$ , MW:84.16) was supplied by RCI-LabScan. L-Arginine (LAG, MW:174.20 g/mol) was supplied by Loba Chemie, India. SiO<sub>2</sub>-NH<sub>2</sub> used in this work was synthesized by cocondensation method under water-CHX biphasic condition [1].

All of membranes in this work were prepared by a dry-wet phase inversion method [2]. Five types of membrane including PSF, PSF/PEG, PSF/PVP, PSF/PEG/SiO<sub>2</sub>-NH<sub>2</sub>, and PSF/PVP/SiO<sub>2</sub>-NH<sub>2</sub>, were fabricated. For pure PSF membrane preparation, 18 g pellet of PSF materials was dissolved in 82 g NMP at 60 °C for 18 h or until PSF completely dissolved. PSF incorporated with PEG and PVP membranes were prepared with the same process by controlling of PEG and PVP content at 1.0, 2.5 and 5.0 wt% of PSF. To fabricate PSF composite membranes in this research, polymeric additives were dissolved in the NMP and pellet of PSF resin was added to the system after the additives completely dissolve in the solvent. SiO<sub>2</sub>-NH<sub>2</sub> in the membrane system was controlled at 1.0 wt% of PSF content. Content of PSF in all membrane was controlled at 18 wt% while the content of NMP depend on the additive loading. To study the alteration of morphological structure and mechanical strength of PSF composite membranes, SEM and DMTA were employed, respectively. Wettability and variation of function groups on the top skin membrane surface were evaluated through the measurement of water contact angle (WCA) and FTIR spectrum.



Figure 1 DMTA result shows the alteration of viscoelastic property of pure PSF membrane (a) and FTIR spectrums show the change of functional groups on top surface of pure and composite PSF membranes (b).



#### **EXPERIMENTAL RESULTS**

<u>Table 1</u>Water contact angles (WCA) of membrane surfaces.

Membrane names	Water c	ontact angle (WCA, °)
Pure PSF	87.35	PSF/SiO <sub>2</sub> -NH <sub>2</sub>
$PSF/SiO_2-NH_2$ (1.0 wt%)	77.72	
$PSF/SiO_2-NH_2/PEG (1 wt\%)$	79.38	PSF/SiO <sub>2</sub> -NH <sub>2</sub> /PEGI.0%
$PSF/SiO_2-NH_2/PEG$ (2.5 wt%)	74.14	
$PSF/SiO_2-NH_2/PEG (5.0 wt\%)$	71.08	PSF/SiO <sub>2</sub> -NH <sub>2</sub> /PEG2.5%
$PSF/SiO_2-NH_2/PVP (1.0 \text{ wt\%})$	79.66	PSF/SiO2-NH2/PEG5.0%
$PSF/SiO_2-NH_2/PVP (2.5 wt\%)$	77.18	
$PSF/SiO_2-NH_2/PVP (5.0 \text{ wt\%})$	76.42	

Figure 2 Cross section of (f) pure PSF, (g) PSF/PEG5%, (h) PSF/PVP5%, (i) PSF/SiO<sub>2</sub>-NH<sub>2</sub> 1%, (j) PSF/SiO<sub>2</sub>-NH<sub>2</sub>/PEG 1.0%, membranes.

SEM-micrographs as shown in figure 2 show the alteration of morphological structure of PSF composite membranes. It was found that macrovoids and sponge-like structure of pure PSF membrane is completely replaced with finger-like structure (red box).

## CONCLUSIONS

Morphology and mechanical strength of PSF can be adjusted by incorporation of inorganic and organics additives into the matrix of membranes. Hydrophilic properties can be controlled by the loading of polymeric (PVP and PEG) additives. Polymeric additives clearly affect the internal structure of PSF membrane was changed from sponge-like structure to the finger-like structure. Macrovoids in pure PSF membrane was replaced by a finger-like structure.

Measurement of WCA results, as shown in table 1 and increase of hydrophilic functional group (OH group), as shown in figure 1(b), on the top surface of PSF nanocomposite membranes confirmed the increase of hydrophilicity. The WCA decrease with increase of polymeric additives.

DMTA results as shown in figure 1(a) confirmed good interaction of polymeric additives and matrix of PSF. Incorporation of PEG and PVP in matrix of PSF lead to decrease of glass transition temperature (Tg). Addition of SiO2-NH2 and PVP can increase  $T_g$  of PSF membrane from 200 °C to about 210 °C. Incontrast, addition of PEG lead to decrease of Tg of PSF membranes.

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