

Physicochemical properties of PSF/SiO₂-NH₂ composite membranes incorporated by polymeric additives

Sunanta thunta and Chalad Yuenyao*

Department of Physics, Faculty of Science and Technology, Phetchabun Rajabhat university, 83 M. 11 Saraburi-Lom sak Road, Sadiang Sub-district, Muang Phetchabun 67000, Thailand

*Corresponding author: chalay_2012@hotmail.com

Abstract: This research project aims to study the effects of PVP and PEG on the morphological structure, hydrophilicity and mechanical properties of PSF/SiO₂-NH₂ composite membranes. To investigate the physical and chemical properties as mentioned, pure PSF and composite of PSF/SiO₂-NH₂ 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/SiO₂-NH₂ composite membranes. Importantly, nano-size pore appeared on the top surface of PSF/SiO₂-NH₂ membranes incorporated with PVP and PEG. Moreover, 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/SiO₂-NH₂, morphological structure, hydrophilic properties, PVP and PEG.

1. Introduction

Polymers, Ceramics, Metal, Carbon and Glass can be used as a thin membrane. Nowadays, most of commercial membranes are fabricated from polymeric materials. A very popular polymer is plastic, synthetic polymer and nowadays, polymers are developed to have good flexibility [1]. In the past decade, membrane separation technology has been widely used in the food industry, medicine, biotechnology because it is a low energy consumption technology, no phase change during separation. Phase inversion process or polymer phase transition is widely used to prepare porous polymer membranes. Polymeric additives with good membrane properties are considered to be quite effective additives. An important effect of inherent hydrophilic additives is to increase the water (hydrophilic) solubility on the membrane surface, stop building a large cavity (macrovoid) and optimization of inter-lockable porosity (interconnectivity). Polyethylene glycol (PEG) is a synthetic chemical in a group of organic substance with high hydrophilic properties. Therefore, PEG is used as an additive to enhance the hydrophilicity of different types of membranes. Polyvinyl pyrrolidone (PVP) can be dissolved in water and other polar solvents. PVP also dissolves in a various types of alcohols such as methanol, isopropanol, ethanol and other solvents. The incorporation of PVP in the dope solution affects the wetting properties of resulted films and make the film easier to form. Silicon dioxide (SiO₂) is used as a catalyst component, used as a strength enhancer and

density in rubber, plastics and polymer products, etc. The amine-added silicon dioxide is intended to make SiO₂ more hydrophilic and more porous.

This research project attempted to study the effects of PVP and PEG on the morphological structure, hydrophilicity and mechanical properties of PSF/SiO₂-NH₂ composite membranes. Pure PSF and composite of PSF/SiO₂-NH₂ 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.

2. Materials and Methods

N-Methyl-2-pyrrolidone (NMP, C₅H₉NO, 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, M_w: 364.45 g/mol) were supplied by Merck, Thailand. Pellet of PSF materials (Udel P-3500 LCD MB) were supported by Solvay, China. Ethanol (EtOH, AR. Grade) and cyclohexane (CHX, C₆H₁₂, MW:84.16) was supplied by RCI-LabScan. L-Arginine (LAG, MW:174.20 g/mol) was supplied by Loba Chemie, India. SiO₂-NH₂ used in this work was synthesized by co-condensation method under water-CHX biphasic condition [1]. All of chemicals were used as received.

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/SiO₂-NH₂, and PSF/PVP/SiO₂-NH₂, 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. SiO₂-NH₂ 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 (or hydrophilicity) and variation of function groups on the top skin membrane surface were evaluated through the measurement of water contact angle (WCA) and FTIR spectrum.

3. Results and discussion

Measurement of WCA results, as shown in table 1, and increase of hydrophilic functional group (hydroxyl; -OH, and carbonyl; -CO, groups), as shown in figure 1, on the top surface of PSF nanocomposite membranes confirmed the increase of hydrophilicity. These results indicated that WCA of membrane surfaces decrease with increase loading of polymeric additives.

Table 1. Water contact angles (WCA) of top skin membrane surfaces.

Membrane names	Water contact angle (WCA, °)
Pure PSF	87.35
PSF/SiO ₂ -NH ₂ (1.0 wt%)	77.72
PSF/SiO ₂ -NH ₂ /PEG(1.0 wt%)	79.38
PSF/SiO ₂ -NH ₂ /PEG(2.5 wt%)	74.14
PSF/SiO ₂ -NH ₂ /PEG(5.0 wt%)	71.08
PSF/SiO ₂ -NH ₂ /PVP(1.0 wt%)	79.66
PSF/SiO ₂ -NH ₂ /PVP(2.5 wt%)	77.18
PSF/SiO ₂ -NH ₂ /PVP(5.0 wt%)	76.42

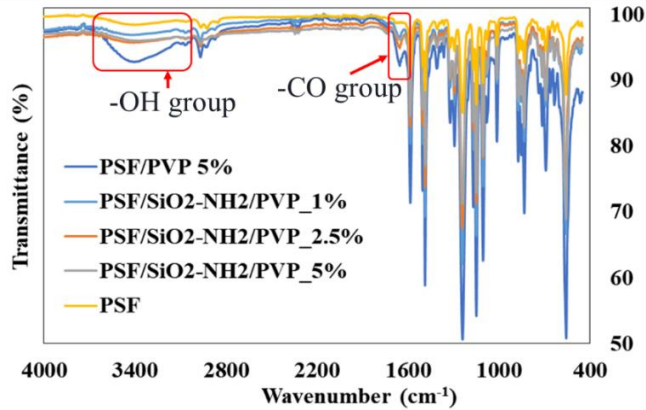


Figure 1. FTIR spectrums show the change of functional groups on top surface of pure and composite PSF membranes.

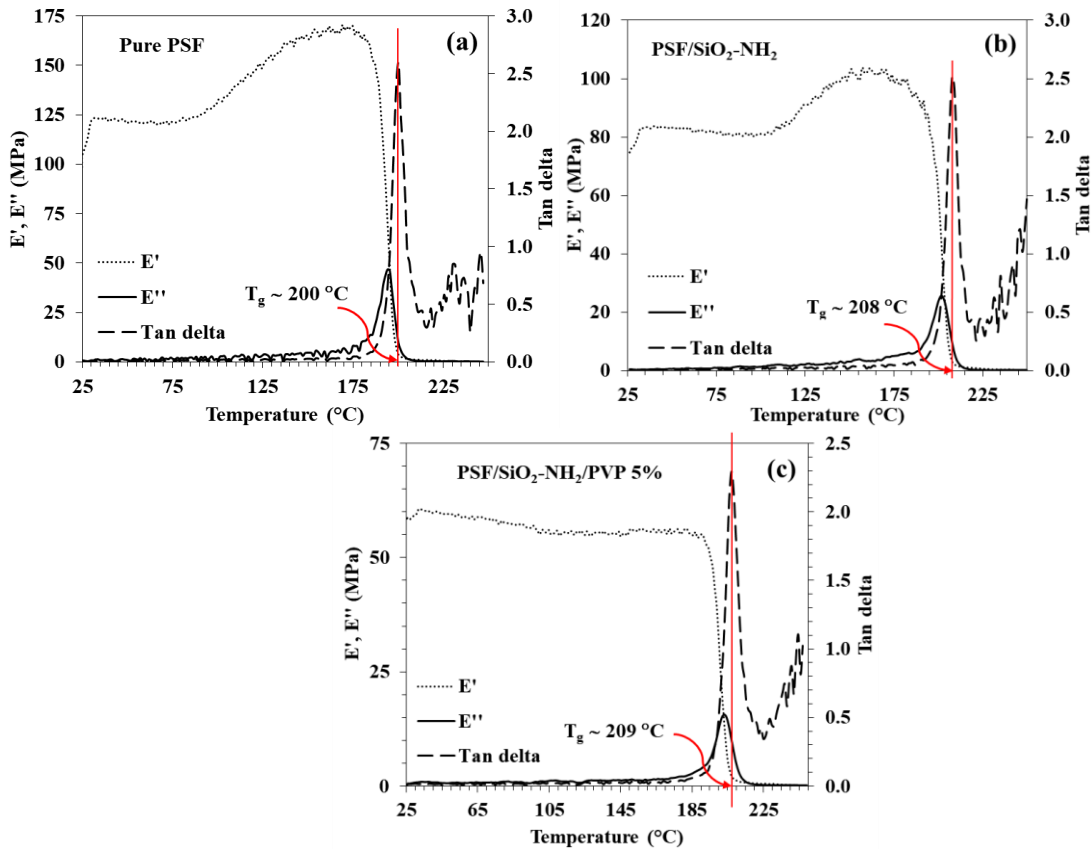


Figure 2. DMTA result shows the alteration of viscoelastic property and glass transition temperature (T_g) of (a) pure PSF, (b) PSF/SiO₂-NH₂ and (c) PSF/SiO₂-NH₂/PVP composite membranes.

DMTA results as shown in figure 2 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 (T_g). Addition of SiO₂-NH₂ and PVP can increase T_g of PSF membrane from 200 °C to about 208 °C and 209 °C, respectively. Incontrast, addition of PEG lead to decrease of T_g of PSF membranes. SEM-micrographs as shown in figure 3 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) when SiO₂-NH₂ nanoparticles, PEG and PVP are incorporated in the matrix of PSF membrane. In addition to the alteration of porous structure as mentioned, top skin layer thickness of PSF/SiO₂-NH₂ composite membranes increase when PEG loading increase from 1.0 to 5.0 wt% as shown in figure 4.

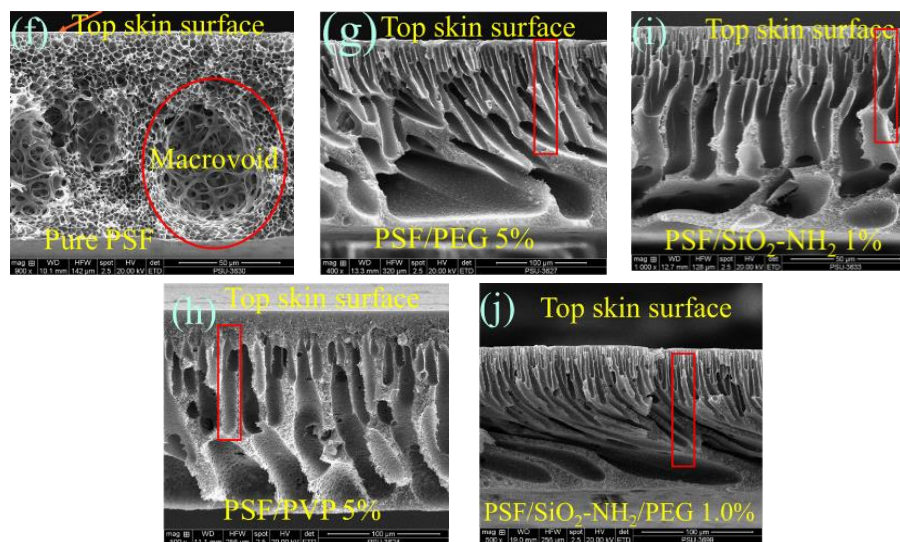


Figure 3. Cross section view of, (f) pure PSF, (g) PSF/PEG 5%, (h) PSF/PVP 5%, (i) PSF/SiO₂-NH₂ 1.0% and (j) PSF/SiO₂-NH₂/PEG 1.0%, membranes.

4. Conclusion

In summary, morphological structures 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. Inorganic nano-porous and polymeric additives clearly affect the internal structure of PSF membrane. Macrovoids in pure PSF membrane were replaced by a finger-like structure in PSF composite membranes. Thickness of top skin layer can be controlled by variation of polymeric additives loading.

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