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Hydrophilicity Effect of Rice Husk Silica on Mixed Matrix PSF Membrane Properties

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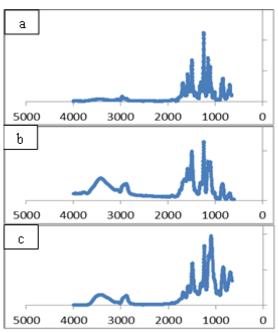
Graphical abstract



Abstract

The effects of two types of additives rice husk silica (RHS) towards membrane hydrophilicity and flux performance were investigated. Different percentages or concentrations of rice husk silica (RHS) additive were used to form a mixed matrix membrane. This flat sheet mixed matrix membrane was prepared via phase inversion technique. The fabricated membrane was characterized by contact angle and surface roughness measurements, whereas the flux permeation was measured using pure water flux. The result demonstrated that the addition both types of rice husk silica have increased the hydrophilicity properties of the mixed matrix membrane. Stronger effect of hydrophilicity is shown upon addition of amorphous rice husk particle where both contact angle and surface roughness were reduced and increased, respectively.

Keywords: Rice husk silica (RHS); Polysulfone (PSf); Polyethelyene glycol (PEG); Pure Water Flux (PWF)

■1.0 INTRODUCTION

Membrane filtration is widely used in numerous sector of industry including water desalination, ultra-pure water production, oil water separation, production beverages, etc [1]. The use of membrane is more dominant than other separation process as its offer low energy consumption, easy scale up, and no harmful by product formation. Ultrafiltration (UF) membrane is one of the most versatile process used to separate a solution including desirable and undesirable components [2-5]. UF membrane process depends on it physical performance such as permeation rate, thickness, mechanical properties and etc. Polysulfone (PSf) membrane is commonly used in UF membrane separation process [2-6]. However, due to its hydrophobicity nature PSf membrane always associated to fouling tendency and low permeation rate. Thus, modification of PSf membrane by introducing of suitable additives to enhance membrane performance, increase hydrophilicity, pore size distribution and also anti-bacterial properties [7, 8] is always preferable. The incorporation of macromolecular additives such as polyethylene-glycol (PEG) into dope solutions is always considered in the formation membrane with higher-porosity and well- interconnected pore structure [8-10]. This pore alteration structure will bring positive implication into membrane performance especially for the flux permeation and fouling mechanism [11-15].

Therefore, in this study the hydroplilic of crystalline RHS and amorphous RHS were used as additives to improve the membrane properties. The effect of silica as additive to improve ultrafiltration membrane is always associated to the hyrophilicity property and have been well documented by several researcher [11, 12]. In fact, the use of RHS form agro-waste product along together of its biodegradable properties will offer better green technology and waste management of agriculture system.

■2.0 EXPERIMENTAL

2.1 Membrane Preparation

Polysulfone (PSf) membranes were prepared by using the phase inversion process via casting method. Casting solution were prepared by dissolving Polysulfone (PSf) in N-methyl-2-pyrrolidone (NMP) and stirred for 4 h. Then, PEG and rice husk silica (RHS) additive at differences concentration (0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.% and 5 wt.%) was subsequently added with continuous stirring and heating at 60°C until the solution was completely dissolved and homogeneous. Meanwhile, two rice husk silica additive was prepared by burning the rice husk in the furnace at temperature range up to 600˚C and 1500˚C then, maintain for 1 h. Subsequently, the casting solution is poured into bottle and ultrasonicated for 1 h to release the bubbles. After the bubbles completely released, the solution were cast by using flat sheet membrane casting system, and then immersed in a coagulation bath of distilled water. Finally, the flat sheet membranes were dried for 24 h.

2.2 Membrane Characterization

2.2.1 Fourier Transport microscopy (FTIR)

FTIR (Perkin Elmer Spectrum 100) was employed to detect and analyze the functional groups within the molecules of the polymer based structure in the prepared membrane. The membranes were characterized using the attenuated total reflectance (ATR) technique at a 4.0 cm^{-1} resolution and the results of 32 scans were recorded

2.2.2 Atomic Force Microscopy (AFM)

The topology of membrane top surface was characterized by using AFM. Each membrane type was cut into small pieces by using sharp razor stainless steel blade, fixed onto magnetic disk by using double sided adhesive tape and then attached to a magnetic sample holder, located on top of the scanner tube. A tapping mode AFM in air was used to take the micrograph. The measurement was performed under ambient atmospheric conditions. At least three separate scans. Each covering 5μm² is acquired for each membrane type to determine roughness values and standard deviations. In order to get a more accurate result, the same sample is used along the measurement.

2.2.3 Contact Angle Measurement

In order to determine hydrophilicity of membrane, the water contact angle (CA) was measured using a Phoenix 300 contact angle analyzer (S.E.O. Co., Ltd, Korea). Ten drops of de-ionized water were measured for each sample at room temperature. The average of measured contact angle was reported as the CA value of the membranes

2.3 Membrane Performance Evaluation

The performance of filtration PSf/PEG ultrafiltration membrane was evaluated based on pure water permeation fluxes (PWF). All the experiments were performed at ambient temperature. The flat sheet membrane was cut in a circle form before it was installed in membrane permeation testing unit cell. The effective area for membrane permeation test was around 2.0 x 10^{-3} cm². The best three membranes with similar thickness and fine surface were prepared for each testing to ensure consistent average value. The pure water flux test was carried out by using distilled water with cross-flow filtration method.

2.3.1 Pure Water Flux Calculations (PWF)

Membrane pure water flux is measured using the following equation.

$$J = \frac{Q}{A.\Delta t} \quad (1)$$

where, Q is the volume permeate (L) , A is membrane surface area m^2 and Δt is permeation time (hour).

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transport Infrared Microscopy (FTIR)

The FTIR spectra of PSf mixed matrix membranes have shown in Figure 1. According to the graph, PSf/PEG (nascent membrane) aromatic vibration ether band was observed around 1239.75 cm^{-1} [16]. The SO_2 group stretching vibration is around 1299 cm^{-1}. PSf also has two methyl groups with vibration at 2969 cm^{-1}. The absorption at 1900.53 cm^{-1}, 1588 cm^{-1}, 1493.89 cm^{-1}, and 1103.11 cm^{-1} are resulted from aromatic ring of PSf. PEG has strong C-O vibration at 2700 cm^{-1} and broad –OH vibration around 3500 [16]. Meanwhile the addition of PEG into PSf was identified by a broad vibration peak at 3500 cm^{-1} and 2700 cm^{-1} [16]. The addition of two types of silica rice husk; crystalline and amorphous show slightly different in FTIR result especially on the–OH vibration as shown in Figure 1. As reported by several research that show silica amorphous structure has slightly shifted of –OH vibration peak (with value at 3471 cm^{-1}) from the crystalline peak (with value at 3500 cm^{-1}) as shown in the figure below [17].

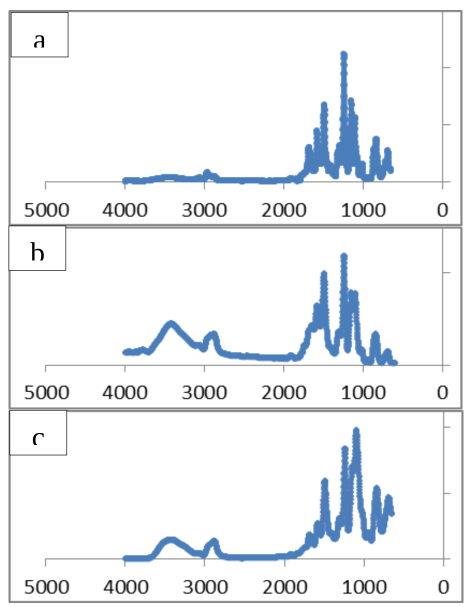


Figure 1 FTIR image: a) PSf/PEG, b) PSf +PEG+Crystalline RHS, c) PSf +PEG+Amorphous RHS

3.2 Membrane Hydrophilicity

In this study, the two types of RHS was added into dope solution which are crystalline and amorphous and its effects on PSf surface hydrophilicity was investigated. The measured contact angle value of crystalline RHS and amorphous RHS membrane are shown in Table 1.

As illustrated in Table 1, the results shows that, the addition of crystalline and amorphous RHS present significant decrement in contact angle value of PSf membrane surface as increases concentration of RHS in the mixed matrix membrane. This indicates that mixed matrix membrane is become more hydrophilic with the presence of RHS for both types RHS particles. Nevertheless, the amorphous RHS demonstrates more hydropilicity effect than crystalline RHS where lower contact angle value is obviously shown when increasing RHS concentration. Comparison between these two types of RHS in mixed matrix membrane at all concentration of RHS reveal that the amorphous RHS has stronger effect of hydrophlicity property. This probably due to the particle of the amorphous has more compatible and similar structure to the polymer structure compared to crystalline RHS [18].

Table 1 Contact angle value of RHS

RHS concentration (wt.%)	Contact angle (˚)	
	Crystalline	Amorphous
0	66.89 ± 0.29	66.89 ± 0.29
1	64.04 ± 0.27	62.81 ± 0.75
2	63.04 ± 0.27	59.88 ± 0.19
3	60.45 ± 0.29	56.97 ± 0.72
4	59.58 ± 0.26	55.38 ± 0.61
5	58.55 ± 0.22	53.98 ± 0.81

3.3 Membrane Surface Roughness

The effect of two different particle towards hydrophilicity of the casted PSf mixed matrix membrane also was measured based on membrane surface roughness. As shown in Figure 2 and Figure 3, both particles show an increase value in surface roughness as increased the RHS concentration. Tremendous changes of surface roughness are shown with amorphous RHS where the highest concentration of amorphous RHS shows the roughest surface morphology. The obvious different in surface roughness could be relate to the effectiveness of hydrophlicity effect of amorphous silica structure compared to crystalline structure, that can attract more water during phase inversion [11, 19]. This mechanism could lead to the instantaneous demixing process and formation of smaller finger-like structure which result in rougher surface morphology [19].

3.4 Membrane Pure Water Flux (PWF)

Figure 4 shows comparison between Pure Water Flux (PWF) for Amorphus and crystalline Rice Husk Silica particle (RHS). The plot demonstrates the amorphous RHS membrane has higher PWF (303.03 LMH) value compared to crystalline RHS membrane (145.45 LMH). It is shows that, PWF for amorphous rice husk silica membrane (RHS) increased as increases concentration of RHS in dope solution from 1 wt.% to 5 wt.%. However, the results is contradicted with crystalline rice husk silica membrane (RHS) which is the PWF reduced as increases concentration of crystalline RHS in dope solution from 3 wt.% to 5 wt.%. This results are aligned with hydoplicity effect that show the value of contact angle and surface roughness is slightly reduced at higher concentration of crystalline RHS, but this is not for the case of amorphous silica. An opposed trend is shown in the amorphous structure where an increase in RHS content lead to the more higher value of hydrophilicity which agree well with higher permeation value. This different in flux permeation can be relate to the different in hydrophilicity value between amorphous and crystalline phases of rice husk particle as mentioned in previous section. As demonstrated and revealed in many related works the enhancement of hydrophilicity property significantly can absorb more water and provide better surface permeation area in membrane structure [18].

4.0 CONCLUSION

In this work, the effect of hydrophicity of two types RHS particle in mixed matrix ultrafiltation membranes towards membranes characteristic and performance were successfully conducted. The presence of amorphous silica particle obviously can enhance hydrophilicity effect of membrane by giving lower contact angle value and higher surface roughness value for all composition of RHS concentration in mixed matrix membrane as compared to crystalline RHS. This better hydrophilicity effect is in sequence with permeation result that show mixed matrix membrane with amorphous silica gives higher value of pure water flux.

Amorphous silica

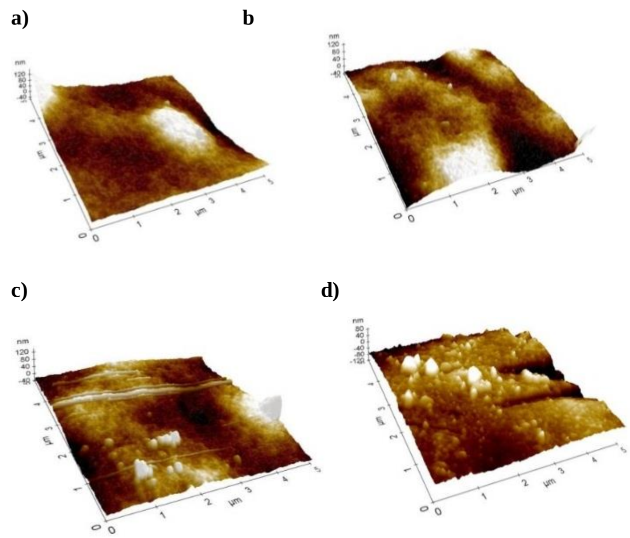


Figure 2 AFM images of PSf/Amorphous RHS membrane : (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.%

Crystalline silica

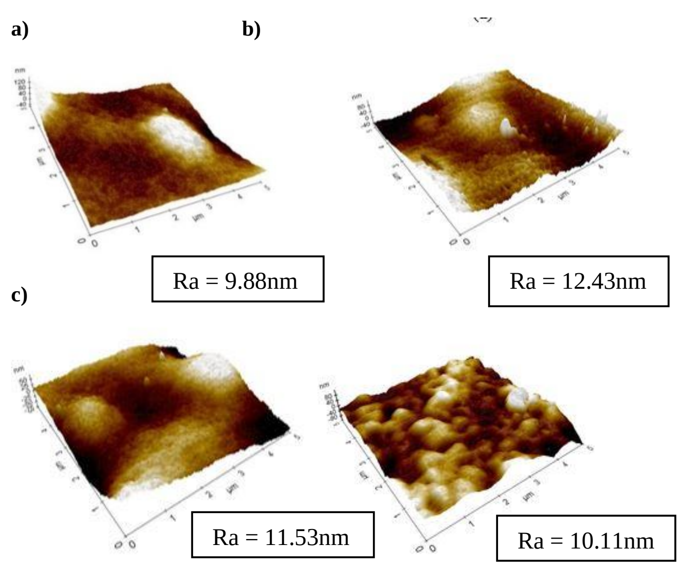


Figure 3 AFM images of PSf/ crystalline RHS membrane: (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.%, (d) 5 wt.%

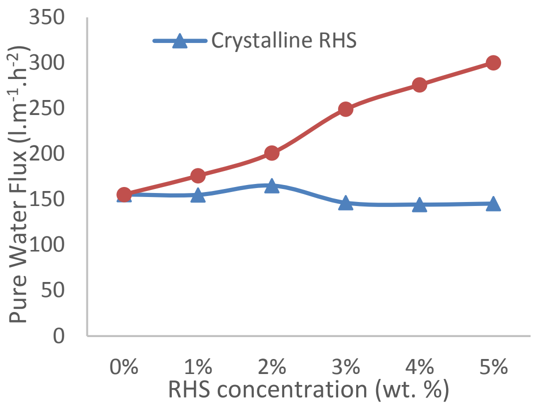


Figure 4 Pure water flux for crystalline RHS and amorphous RHS

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