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To cite this article: C Kaew-on *et al* 2021 *J. Phys.: Conf. Ser.* **1719** 012112

Modifying surface properties of polysulfone membrane with plasma from closed and opened plasma generators

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Abstract. Plasma jet has been widely used in the process of surface modification. However, the operation process often operates in an opened plasma jet system. This research investigated surface modification of flat-sheet polysulfone membrane by using three different types of atmospheric pressure cold plasma jet system that comprised of plasma jet in an opened system, in a closed system and in a closed with pump out plasma gas system. This research aims to improve surface wettability of membrane surfaces. The samples were irradiated with argon plasma in such three systems. The properties of the treated membranes were verified by measuring Water Contact Angle (WCA), Surface Energy (SE) and surface roughness. The results show that plasma jet in the closed with pump out plasma gas system provided the best results due to its lowest water contact angle, the highest surface energy and the highest surface roughness.

1. Introduction

Polysulfone (PSF) is a thermoplastic material that uses in many applications, including membrane applications since it has many advantages such as high resistance to chemical and physical change and thermal stability [1,2]. Many applications such as gas separation and water purification use PSF as a membrane in the process [3,4]. However, it is necessary to change its surface property from hydrophobicity to hydrophilicity for optimal condition. Many methods have been used to change its properties such as surface coating, chemical coupling, polymerization, UV and gamma irradiation [5]. Plasma surface modification is a method that use plasma particles and plasma energy from low pressure or atmospheric pressure plasma generator to modify membrane surface [6-7]. Many researchers use plasma jet in the process of surface modification since it has many advantages such as no vacuum system, low cost and easy to use [8]. However, membrane surface modification using plasma jet usually operates in an opened system that may affect by surrounding environment such as humidity and type of working gas.

This research had investigated the effect of plasma jet system in the process of PSF membrane surface modification by using plasma jet in an opened system, a closed system and a closed with a pump-out system.

2. Methodology

The process of investigation comprises of four parts; membrane preparation, plasma generation, plasma treatment and membrane verification.

2.1. Membrane preparation

PSF membranes were prepared by using dry/wet phase inversion technique. The 22.00 wt% dried PSF pellets that prepared in a vacuum oven at 70 °C for 24 h were mixed in the dope solution that comprised of 31.05 wt% DMAC, 31.05 wt% THF and 15.90wt% EtOH in a beaker. The mixed substance was stirred on a magnetic stirrer for 24 h at room temperature. The bubbles in the dope solution were removed by using an ultrasonic machine for 30 min and resting in an open-air for 1 h before casting on a clear glass plate with a thickness of 150 µm and resting 120 s in ambient air. The prepared membrane was immersed in RO-water for 15 min before immersing in MeOH for 2 h. Finally, the prepared membrane was dried by hanging in an opened air at room temperature for 24 h before using.

2.2. Plasma generation

Plasma jet was generated by using a plasma jet system that comprises the RF power supply unit, gas supply unit and plasma generator unit, as shown in figure 1 (a). The plasma generator unit that connected with a power supply unit and a gas supply unit comprises of a floating electrode and a Pyrex glass tube. Before the plasma treatment process, the plasma jet system was pre-tested by flowing argon gas with a flow rate of 5 L/min to the plasma generator unit. Then, the power supply was adjusted to 40 W to generate plasma jet, and the power frequency was adjusted to get the optimal condition for plasma generation. At the optimal state, plasma discharge will create high plasma density that can be seen by the naked eye.

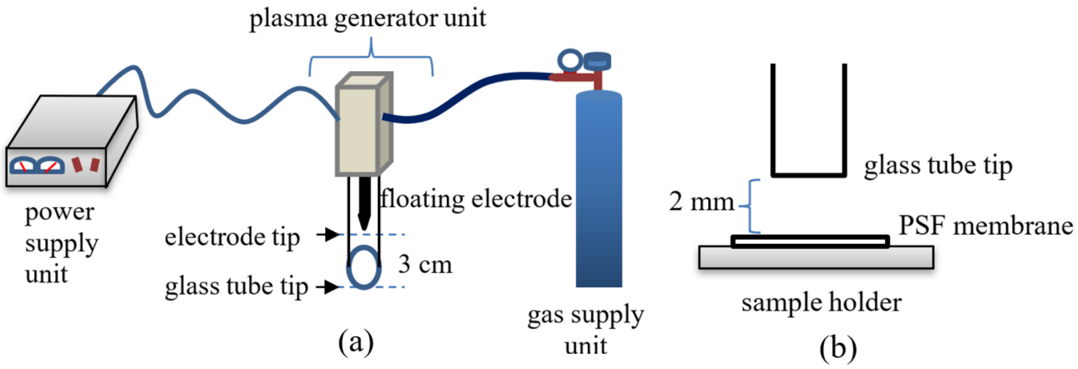

Figure 1. Experimental setup: (a) compositions of the plasma jet system and (b) surface plasma treatment setup of PSF membrane.

2.3. Plasma treatment

The membrane samples were treated using three different systems. The first step of the plasma treatment process for each condition, the PSF flat-sheet membrane sample was struck on a sample holder and was set at around 2 mm under the tip of the plasma glass tube as shown in figure 1 (b). After that, argon gas flowed to the plasma generator unit and, then, the power supply was turned on to generate plasma at the optimal condition. The membrane sample was treated for 60 s and, then was placed in an opened air before the verification process. For plasma treatment in an opened system, the membrane sample was placed in the open air, as shown in figure 2 (a). For plasma treatment in a closed system, the membrane was placed on a sample holder at the middle part inside a cylinder tube with a diameter of 10 cm and height of 16 cm as shown in figure 2 (b). For plasma treatment in a closed with a pump-out plasma gas system, the membrane was struck on a sample holder in the middle part of the cylinder tube. At the downside of the cylinder tube, the rubber hose was connected at the hole for air pumping by using a one-way air pump, as shown in figure 2 (c). While treating the membrane sample, the air in the closed system was pump out from the system immediately.

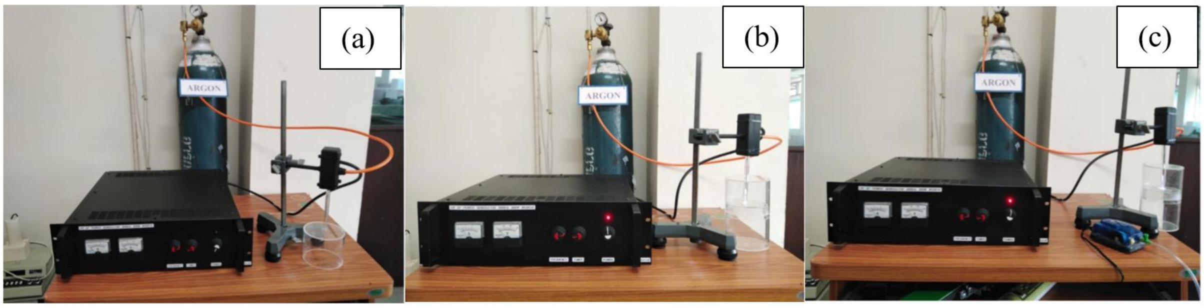

Figure 2. Surface modification of PSF membrane using three different systems: (a) opened system (b) closed system and (c) closed with pump-out plasma gas system.

2.4. Membrane verification
The surface wettability of PSF treated membranes was verified by measuring the water contact angle (WCA), surface energy (SE) by using water contact angle machine and measuring the surface roughness from root means square (RMS) thickness by using atomic force microscope (AFM).

3. Results and discussions
The results from measuring of WCAs, SE and RMS thickness was shown in table 1. These results have been used to identify surface wettability of the untreated and the treated PSF membrane surface due to different types of plasma jet property system as the following details.

Table 1. WCA, SE and RMS thickness of the membrane surface from different plasma jet system.

Material	Average WCA (degree)	Std (degreees)	SE (mJ/m^2)	Dispersive (mJ/m^2)	Polar (mJ/m^2)	RMS thickness (nm)
U-PSF	76.82	2.53	29.13	14.65	14.48	29.94
O-PSF	73.12	1.64	35.76	23.24	12.52	26.63
C-PSF	72.78	2.12	36.36	25.38	10.98	30.69
CF-PSF	61.40	1.74	40.03	18.43	21.60	36.21

3.1. Water contact angle
The results of WCAs shown in table 1 reveal that the surface of the treated membrane from different plasma jet system gave different results. The untreated PSF (U-PSF) membrane had an average WCA of 76.82 ± 2.53 degrees, while the opened plasma jet system (O-PSF) and the PSF treated in the closed plasma jet system (C-PSF) had the average WCA of 73.12 ± 1.64 degrees and 72.78 ± 2.12 degrees, respectively. These results mean that PSF membrane surface can be improved surface wettability by using a plasma jet. However, the PSF membrane surface treated by using the plasma jet in a closed with a pump-out plasma gas inside the system all operating time (CF-PSF) shows excellent results. This method gave the lowest WCA that decreased from 76.82 ± 2.53 degrees to 61.40 ± 1.74 degrees. Since the plasma energy can cause the chemical bond at the membrane surface to be cut and reconstructed, so, the hydrogen atoms at the polymer surface can be replaced by other atoms or molecules to construct new atoms or molecules on the membrane surface[9]. The reaction between atoms of the treated PSF membrane surface and oxygen-containing groups in an atmosphere of the jet plasma can introduce hydrophilic groups at the treated membrane surface, leading to an increase in the wettability of the membrane surface [10]. So, the CF-PSF method may cause the highest plasma density at the membrane surface, leading to the highest interaction between plasma particles and atoms or molecules at the polymer membrane surface.

3.2. Surface energy
Surface energy (SE) was used to identify the surface properties of the membrane surface. SE of the treated PSF membrane surfaces was measured by using water contact angle machine with the different type of a liquid drop. The results shown in table 1 reveal that the SE of the U-PSF had an average SE of 29.13 mJ/cm^2, while the SE of O-PSF and C-PSF had the average SE of 35.76 mJ/cm^2 and 36.36 mJ/cm^2, respectively. These results show that the PSF membrane surface can improve surface wettability by using a plasma jet. However, the SE of CF-PSF was 40.03 mJ/m^2 that was higher than both the other two systems. These results have corresponded to the results of WCA.

3.3. Surface roughness
Surface roughnesses of the treated PSF membrane surface were investigated by using atomic force microscope (AFM). The surface roughness of each condition was shown in figure 3. The results show that the root means square (RMS) thickness value of U-PSF in figure 3 (a), O-PSF in figure 3 (b) and C-PSF in figure 3 (c) were 29.94 nm, 26.63 nm, 30.69 nm, respectively. While the RMS thickness value of CF-PSF in figure 3 (d) had the highest value of 36.21 nm. This means that the CF-PSF method can cause the highest surface roughness and lead to the highest surface wettability of the treated membrane. These results have corresponded to both the results of WCA and SE.

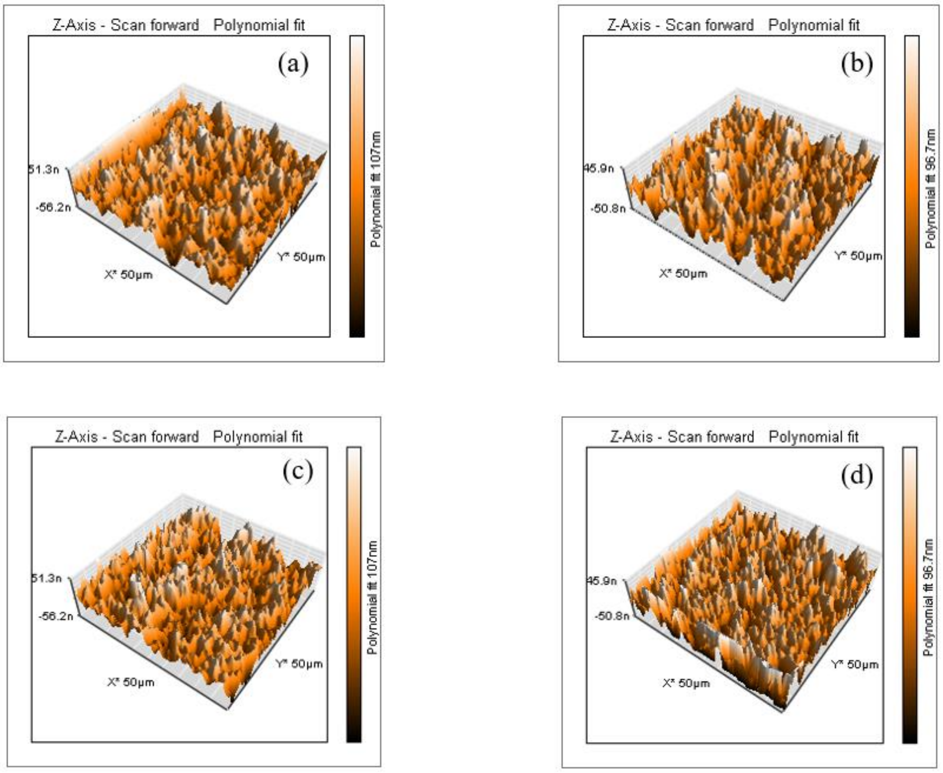

Figure 3. The surface roughness of PSF membrane from different conditions, (a) U-PSF, (b) O-PSF, (c) C-PSF and (d) CF-PSF.

4. Conclusion
Surface modification of PSF membranes by using plasma jets at different conditions provide different results. The CF-PSF membrane surface had the best results among other treated membranes. This results may imply that plasma jet in a close with a pump-out plasma gas system can improve the WCA and SE of the PSF better than a closed system and an opened system.

Acknowledgements
The authors would like to thank the faculty of Science and Technology, Nakhon Si Thammarat Rajabhat University and Center of Excellence in Membrane Science and Technology, Prince of Songkla University, for supporting facilities.

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