Chapter 10

Polysulfone/Cellulose Acetate Phthalate/Polyvinylpyrrolidone (PSf/CAP/PVP) Blend Membranes: Effect of Evaporation Time on Blend Membrane Characteristics

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Abstract Recently, researchers proved that the evaporation time during the membrane fabrication process has a significant effect on the characteristics and performance of membranes. In this study, flat sheet asymmetric polysulfone/cellulose acetate phthalate/polyvinylpyrrolidone (PSf/CAP/PVP) blend membranes were fabricated at different evaporation time in the range of 0–20 s to investigate the effect of the evaporation time on characteristics of the blend membranes. The PSf/CAP/PVP blend membranes were characterized in terms of water content, porosity, pure water flux and permeability coefficient. The results showed that an increase of evaporation time from 0 to 20 s has resulted in decreasing of water content and porosity of the PSf/CAP/PVP blend membranes. The permeation water flux of the blend membrane

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was decreased with the increment of evaporation time. This indicated that an increase of evaporation time would lead to a decrease of the membrane permeability coefficient and hence increased the membrane resistance to permeation of water through the membranes.

Keywords Ultrafiltration · Evaporation time · Blend membrane · Flux

10.1 Introduction

In recent years, membrane technology has been accepted as one of the best available alternative technologies that can be offered to treat the contaminated water from pollutants. This technology is being employed at water treatment plants for producing a high quality of drinking water to comply with a specified standard before it can be supplied to the customer. Ultrafiltration (UF) is one of the promising membrane technology processes that have been received much attention in water treatment process as an effective technology in the removal of suspended solids, colloidal material, inorganic particulates and fatal microorganisms. Most of the commercial membranes used in the UF membrane technology process is an asymmetric membrane and this type of membrane can be fabricated to suit with their suitable application in the water treatment process.

The invention of the asymmetric membranes by Loeb and Sourirajan since 50 years ago has made a great impact on the growth of membrane science and technology. Their breakthrough has put a milestone in the history of membrane technology progress. This remarkable finding has opened the door to commercialize the membrane technology from laboratory-scale membrane application turn to large-scale commercial [1]. Nowadays, most of the commercial membranes have been fabricated by using the phase inversion method. In the phase inversion process, membrane casting solution is changed to a solid thin membrane film by the dry–wet phase inversion technique. During this technique, the membrane casting solution which contains a polymer and a solvent is poured on a plate and cast by a casting knife to produce a thin membrane film [2]. The film is introduced to dry air or nitrogen gas to evaporate the solvent from the membrane film solution for a certain period of time that is known as the evaporation time. Then, the partial solid of thin membrane film is immersed into a coagulation bath to complete the membrane fabrication process [3].

Nowadays, a few of studies by researchers proved that the evaporation time, as one of the important membrane fabrication parameters affects the asymmetric membrane characteristics, morphology and performance of polyethersulfone (PES), polyaniline (PAni) and BDTA-TDI/MDI co-polyimide (P84) membranes in gas separation process [4–6]. In the ultrafiltration (UF) membrane separation process, the separation performance of the UF membrane is solely related to the characteristics and structural morphology of the UF membranes. Hence, in this study flat sheets of PSf/CAP/PVP blend UF membranes were fabricated at different evaporation times to alter their characteristics of the blend membranes. The UF blend membranes were characterized in terms of water content, porosity, pure water flux and permeability coefficient.

10.2 Methodology

10.2.1 Materials

All materials used were of analytical grade. The PSf/CAP/PVP blend membranes were fabricated from ternary casting solutions which consist of PSf (supplied by Amoco Chemical (USA) S. A.) as the membrane backbone polymer, CAP (purchased from Sigma-Aldrich Co.) as the hydrophilic polymer, *N*-Methyl-2-Pyrrolidone (NMP) from MERCK Schuchard OHG (Germany) was used as solvent and polyvinylpyrrolidone (PVP) K15 was purchased from Fluka employed as an organic additive. Distilled water was used as the coagulation bath medium.

10.2.2 Membrane Preparation

The casting solutions of asymmetric PSf/CAP/PVP blend membranes were prepared consisting of 17 wt% of polymer composition (PSf/CAP), 3 wt% of PVP additive and 80 wt% of NMP solvent in the total membrane casting solution. CAP contained 10 wt% in total polymer composition as explained by Ali et al. [1]. The casting solutions were poured onto a stainless steel plate, and then, they were cast by using an automatic casting machine. The cast polymer solutions were introduced with a convective inert stream (nitrogen) for a certain period of time which is known as evaporation time in the dry-phase inversion process.

After that, the cast polymers were immersed in a coagulation bath in order to complete the formation of solid flat sheet membranes. The prepared membranes were stored in distilled water prior usage. In this study, the evaporation time was studied in the range of 0, 5, 10, 15 and 20 s and the produced blend membranes were marked as PCE-0, PCE-5, PCE-10, PC-15 and PCE-20 membranes, respectively.

10.2.3 Membrane Characterization

10.2.3.1 Water Content and Porosity

The water content of the PSf/CAP/PVP blend membranes was evaluated for water absorption capacity and calculated by Eq. (10.1):

$$A = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}}, \tag{10.1}$$

where A is the water content (wt%), W_{wet} is the wet weight of membrane (mg), and W_{dry} is the dry weight of membrane (mg). The water content of the membranes was determined by soaking the membranes in water for 24 h at room temperature. The weight of the wet PSf/CAP/PVP blend membranes was first measured after mopping the membranes with a blotting paper and then dried in an oven at 75 °C for 48 h. The porosity of PSf and PSf/CAP blend membranes was evaluated using the expression below:

$$\text{porosity} = \frac{(W_1 - W_2)/d_{\text{water}}}{V}, \tag{10.2}$$

where W_1 and W_2 are the mass of membrane in wet and dry states (mg), d_{water} is the density of water at room temperature (ml/mg), and V *is* the volume of the membrane in wet state (ml).

10.2.3.2 Pure Water Flux and Permeability Coefficient

Pure water flux is important for the determination of the membrane stability and hydraulic properties. Distilled water was used to determine the pure water flux of each PSf/CAP/PVP blend membranes using a dead-end filtration cell. Membranes were then subjected to a pure water flux test with varying operating pressure in the range of 1–5 bar. The membrane permeability coefficient of PSf/CAP/PVP blend membranes can be determined by subjecting these membranes at various pressures towards its pure water fluxes. The effect of the evaporation time on the hydraulic permeability coefficient of PSf/CAP/PVP blend membranes is determined from the slope of the linear line of pure water fluxes.

10.3 Results and Discussion

10.3.1 Water Content and Porosity

Table 10.1 shows the water content and porosity of the PSf/CAP/PVP membranes which were introduced to evaporation time during the membrane fabrication process. It was observed that the water content and porosity of the PSf/CAP/PVP membrane in the absence of evaporation time shows the highest value compared to the blend membranes introduced to the evaporation time. The PSf/CAP/PVP membranes introduced at low evaporation time have higher water content and porosity compared to the blend membrane fabricated at high evaporation time. It was observed that an

Table 10.1 Effects of evaporation time on water content and porosity of PSf/CAP/PVP blend membranes

Membrane	Evaporation time (s)	Water content (%)	Porosity (%)	Permeability coefficient (l/m^2 h bar)
PCE-0	0	78.13	74.59	66.14
PCE-5	5	75.20	69.73	56.64
PCE-10	10	74.93	68.98	47.55
PCE-15	15	72.78	64.22	34.32
PCE-20	20	70.44	62.84	27.31

increase in evaporation time significantly decreased the water content and porosity of the PSf/CAP/PVP blend membranes as given in Table 10.1.

Ohya et al. [7] and Sabri et al. [8] studied the effect of evaporation time on asymmetric aromatic polyimide membranes. They found that shortening the evaporation time will decrease the evaporated quantity of solvent and consequently change the polymer concentration at the polyimide surface which in turn produced membranes with big pore size and high porosity. Ali et al. [6] found the formation of larger pores in blend membranes increased the porosity of the PSf/CAP blend membranes. Based on the results from Table 10.1, it was postulated that a decrease in water content and porosity of PSf/CAP/PVP blend membranes which were fabricated at high evaporation time due to the formation of small pore size at the membrane surfaces. Generally, membranes with small pore size have a high resistance and lower porosity to water to absorb through the membrane structures which in turn decreased the water content of UF membranes.

10.3.2 Pure Water Flux and Membrane Permeability Coefficient

The measurements of pure water permeation as a function of applied pressure were used to investigate the stability and hydraulic properties of UF membranes. Figure 10.1 represents the influence of the evaporation time on the pure water flux of the PSf/CAP/PVP blend membranes measured at various operating pressures in the range of 1–5 bar. As shown in Fig. 10.1, pure water flux was a linear function of the applied pressure. The PSf/CAP/PVP blend membrane in the absence of evaporation time (PCE-0), i.e., the casting solution film which was immediately immersed into a coagulation bath exhibited the highest range of pure water flux in the range of 72.63–318.90 l/m^2 h.

As shown in Fig. 10.1, the trend of the linear line of the pure water flux was decreased by increasing the evaporation time introduced to the casting solution films. The PSf/CAP/PVP membrane introduced to 20 s of evaporation time (PCE-20) shows the lowest pure water flux in the range of 25.02–140.39 l/m^2 h. It was observed that the decrease in pure flux was proportional to the evaporation time. The results revealed

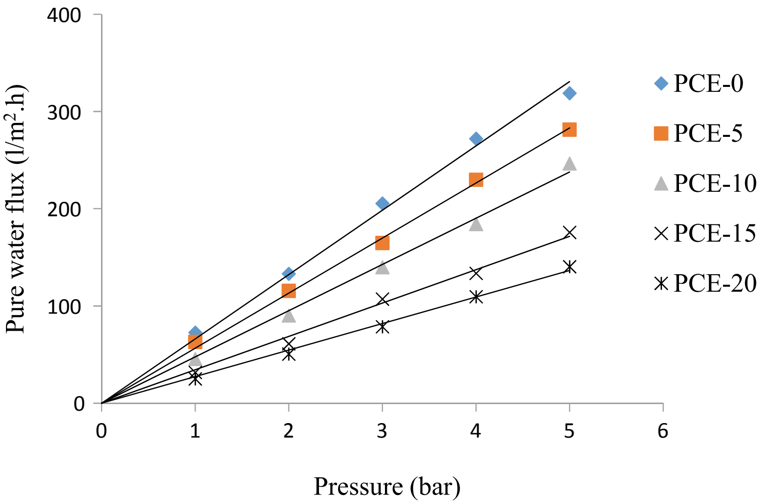

Fig. 10.1 Pure water flux of PSf/CAP/PVP blend membranes fabricated at different evaporation time at the operating pressure of 1–5 bar

that the order of pure water flux of PSf/CAP/PVP blend membranes was decreased as to be PCE-0 > PCE-5 > PCE-10 > PCE-15 > PES-20. The permeability coefficient of five tested membranes of PCE-0, PCE-5, PCE-10, PCE-15 and PCE-20, respectively, can be obtained from the slope of the straight line in Fig. 10.1 and provided in Table 10.1.

Membrane in the absence of evaporation time (PCE-0) exhibited the highest membrane permeability coefficient of 66.14 l/m^2 h bar. However, an increase in the evaporation time from 5 to 20 s gradually decreased the permeability coefficient of PSf/CAP/PVP blend membranes from 56.64 to 27.31 l/m^2 h bar. Noticeably, the permeability coefficient of membranes decreased in the following sequence: PCE-0 > PCE-5 > PCE-10 > PCE-15 > PCE-20. This indicated that an increase of evaporation time would lead to a decrease in the membrane permeability. In other words, an increase in the evaporation time of membrane produced membranes with high membrane hydraulic resistance characteristics and low porosity which in turn decreased the water permeation flux.

According to Huang and Feng [9], the increment in evaporation time removed the most volatile solvent from the membrane surface and led to form more a concentrated nascent skin layer. During the evaporation process, the thickness of the skin layer was a function of time and rate of solvent evaporation. An increasing in the evaporation time induced high evaporation rate of the most volatile solvent and consequently increased the polymer concentration at the nascent skin membrane which in turn formed a thick skin layer. Hasbullah et al. [4] reported that the skin layer thickness was increased with the increase of evaporation time. Jami'an et al. [10] also revealed that an increase of evaporation time produced a membrane with a compact sublayer which contributes to the high resistance to gas molecules to penetrate through membrane layer.

Based on Fig. 10.1 and Table 10.1, it was proven that the pure water flux depends on the membrane permeability coefficient and porosity. It was suggested that the PSf/CAP/PVP blend membranes prepared at high evaporation time produced membranes with thicker skin layer due to higher polymer concentration at the membrane skin layer than the membranes fabricated at low evaporation time. It was due to the increase in the polymer concentrations at the nascent skin layer which tend to increase thickness and dense of the membrane, which consequently results in a low hydraulic permeability, high hydraulic membrane resistance and low porosity. Ismail's et al. [3] and Benhabiles's et al. [11] observed the same results for PES membranes. It was also postulated the sublayer of the membrane also appears in compact structure due to decrease in solvent evaporation rate.

10.4 Conclusion

The results showed that the effects of evaporation time significantly changed the characteristics of the PSf/CAP/PVP blend membranes in terms of water content, porosity, pure water flux and permeability coefficient. The results revealed that an increase of evaporation time has decreased the water content and porosity of the blend membranes. It was postulated that the membranes fabricated at high evaporation time formed membranes with small pores which in turn resist water to absorb through the pores and consequently reduced the water absorption and porosity. It was also observed that the decrease in pure water flux was proportionate to the evaporation time due to decrease in permeability coefficient and the increment of hydraulic membrane resistance of the PSf/CAP/PVP membranes. This study revealed that the fabrication of different UF membrane characteristics was successfully developed by manipulating the evaporation time and these membranes are potentially used for a wide range of water treatment process.

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