The Effects of Evaporation Time on Morphological Structure of Polysulfone/Cellulose Acetate Phthalate/Polyvinylpyrrolidone (PSf/CAP/PVP) Blend Membranes

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Abstract. Evaporation time is one of the important membrane fabrication parameter that can be manipulated in order to produce the desired membrane morphology in ultrafiltration (UF) separation process. The morphology of UF membrane has a significant effect on structural properties and performance of UF membrane. In this study, flat sheet asymmetric polysulfone/cellulose acetate phthalate/polyvinylpyrrolidone (PSf/CAP/PVP) blend membranes were prepared at different evaporation time in the range of 0 to 20 s to investigate its effect on the morphological structures of the blend membranes. The morphological structure of these blend membranes were characterized by using Scanning Electron Microscopy (SEM). The results showed that in the absence of evaporation time, the morphology of blend membrane consits of open finger-like structure and microvoids. Introduction of evaporation time period between 5 to 10 s, produced spongy blend membranes with less finger-like structure. Further increment of evaporation time between 15 to 20s, formed incomplete dense structure with small microvoids PSf/CAP/PVP blend membranes.

Introduction

Nowadays, most commercial available membrane obtained by phase inversion. It is a process whereby a polymer is transformed in a controlled manner from a liquid to a solid state. The simplest technique for preparing phase inversion membrane is precipitation by solvent evaporation. In this method a polymer is dissolved in a solvent and the polymeric solution is cast on a suitable support. The solvent is allowed to evaporate in an inert atmosphere in order to exclude solvent from the polymeric solution to form a dense homogeneous membrane. This inversion method is known as dry phase inversion. The time required to evaporate solvent from the polymeric solution during membrane fabrication process is known as evaporation time[1].

There are many researchers studied on the effects of evaporation time during dry phase inversion process on membranes characteristics and performance. It is due to different membrane morphology and properties can be obtained for tailor-made membranes by varies the evaporation time. The integrally skinned asymmetric membrane can be developed by introducing dry phase inversion for polymer casting solution before wet phase inversion technique take place during fabrication of asymmetric membranes. The combination of these two techniques was reported successful in producing membrane with high productivity and selectivity.

Recently, a few researchers reported the effects of evaporation time on properties, morphology and performance of polyethersulfone (PES), polyaniline (PAni) and BDTA-TDI/MDI co-polyimide (P84) membranes which prepared via dry-wet phase inversion process technique in gas separation process [1-3]. During fabrication of these membranes, different evaporation time were performed which resulted membranes with different morphological structures and characteristics which in turn affect the membrane performance. In ultrafiltration (UF) membrane separation process, the separation performance of UF membrane related to the structural properties and morphological structures of the membrane. An extensive literature survey revealed that there is no published document discussed about the effects of different evaporation time on morphological structure of PSf/CAP/PVP blend UF membrane. In view of this, flat sheets PSf/CAP/PVP blend UF membranes were fabricated at different evaporation time to alter the morphology of the blend membrane. The morphology of UF blend membranes were characterized by using scanning electron microscopy (SEM) in order to investigate the role of evaporation time effects on the morphological structure of the blend membrane.

Materials and Methods

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 membrane back-bone polymer, CAP (purchased from Sigma-Adrich Co.) as 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 coagulation bath medium.

Membrane Preparation. The casting solutions of asymmetric PSf/CAP/PVP blend membranes were prepared consist 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's et al. [4]. The casting solutions poured onto a stainless steel plate and then, they were cast by using an automatic casting machine. In order to study the effects of evaporation time on morphology of the blend membranes, dry-phase inversion method was introduced before wet-phase inversion process took place during preparation of PSf/CAP/PVP blend membranes. In the dry phase inversion method, the cast polymer solution was introduced with a convective inert stream (nitrogen) for a certain period of time which is known as evaporation time. During this evaporation time, the convective stream removed the most volatile solvent from membrane surface, which results in a region with locally elevated polymer concentration at the nascent membrane surface. The complete phase inversion process was followed by wet-phase inversion method which the blend membranes were immersed into a coagulation bath for 24 h to remove excess solvent in the fabricated membranes after dry phase inversion performed. 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.

Membrane Morphology. The Scanning Electron Microscopy (SEM) (JSM P/N HP475 model) at Institute of Oceanography, Universiti Malaysia Terengganu (UMT) was used to analyze morphological structures of PSf/CAP/PVP blend membranes. SEM was used to inspect the cross-section of the fabricated membranes. The membrane samples were fractured in liquid nitrogen and sputtered with gold, before transfer and analyze by using the microscope.

Results and Discussion

Scanning Electron Microscopy (SEM) is important for the determination of morphology of the membranes. Figure 1 shows the images of cross-sectional morphological structures of PSf/CAP/PVP blend membranes by scanning electron microscopy (SEM). Generally, all the fabricated blend membranes comprise of a good asymmetrical structure of skin and sub-layers.

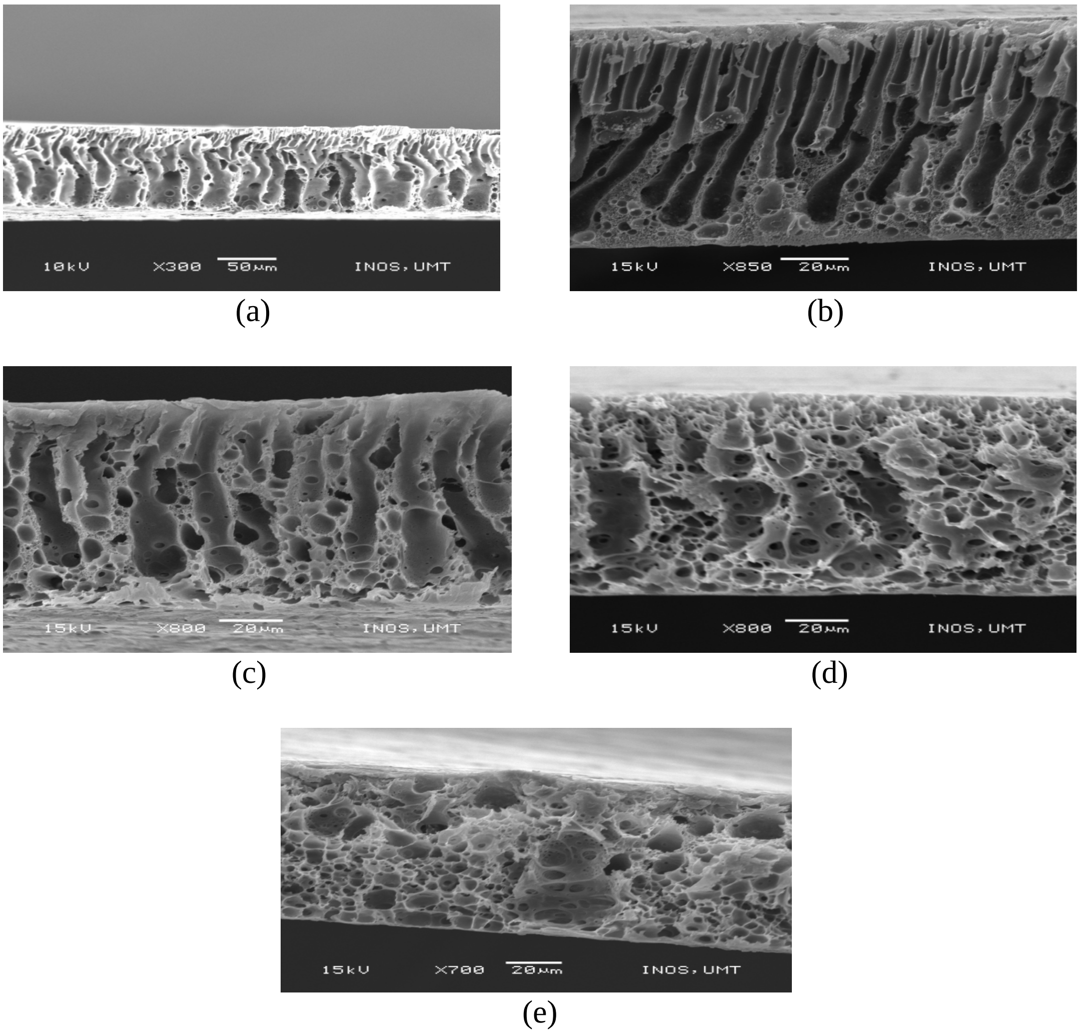

Fig. 1: Cross section of membrane morphology of PSf/CAP/PVP blend membranes at various evaporation time;
(a) PCE-0; (b) PCE-5; (c) PCE-10; (d) PCE-15; (e) PCE-20

Figure 1(a) shows the SEM photograph of the membrane in absence of evaporation time (PCE-0). It can be seen that the cross-section of morphological structure of PCE-0 membrane had an open finger-like structure and macrovoids. An introduction of evaporation time for 5 s significantly changed the morphological structure of the PSf/CAP/PVP blend membrane as depicted in Figure 1(b). It was observed that the open finger-like structure presence in the PCE-0 membrane without evaporation time became narrow finger-like structure and it was noticed that the existence of dense layer with small microvoids at the bottom sub-layer. It was observed that the presence of thicker skin layer of PCE-5 membrane compare to PCE-0 membrane.

Further increment of evaporation time from 5 to 10 s decreased the number of finger-like structure and developed more spongy structure with the presence of small microvoids as displayed in Figure 1(c). As depicted in Figure 1(a) to 1(c), the skin layer thickness became thicker which indicated that the skin layer thickness was increased by increasing the evaporation time and consequently enhanced the membrane hydraulic resistance; this in turn may reduced the pure water to permeate through the PSf/CAP/PVP blend membranes. Figure 1(d) and (e) illustrate SEM photographs of cross-sectional view of PSf/CAP/PVP membranes prepared at 15 and 20 s of evaporation time. As the evaporation time increased in the range of 15 to 20 s, the entire membrane structure was changed. It was observed that the finger-like structures were diminished and the incomplete dense structure was formed with the presence of small microvoids. Further increment evaporation time from 15 to 20 s reduced macrovoids structure presence in the sub-layer of PCE-20 membrane as depicted in Figure 1(e).

The change of morphological structure of membrane with an increasing evaporation time was due to movement of volatile solvent at casting film surface. The increasing evaporation time removed more volatile solvent from membrane surfaces. In this phenomenon, a homogeneous and more concentrated nascent skin layer was formed due to coalescence and fusion of dry phase-separated structure. This type of nascent skin layer had high resistance to mass transfer of solvents and non solvents between the coagulation bath and the interior region of membrane during the wet phase inversion process [5]. The resistive top layer caused a delayed phase separation before solidification in sub-layer and consequently, asymmetric membranes with a dense and thick skin layer supported by a closed-cell substructure were formed at high evaporation time [4].

Conclusions

The results show that the effects of evaporation time significantly changed the morphological structures of the PSf/CAP/PVP blend membranes. In absence of evaporation time (or dry inversion technique), the morphology of PSf/CAP/PVP (PCE-0) blend membrane had an open finger-like structure and macrovoids. Introduction of 5 s of evaporation time produced PCE-5 blend membrane with narrow finger-like structure. An increment of evaporation time from 5 to 10 s decreased the number of finger-like structure and developed more spongy structure with the presence of small microvoids. Further increment evaporation time from 15 to 20 s produced PCE-15 and PCE-20 blend membranes with incomplete dense structure with small microvoids due to a delayed phase separation occured during dry-wet phase inversion technique.

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