MTE-4

Concentration influence of different additives on performance of asymmetric polyethersulfone (PES) ultrafiltration flat sheet membranes

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Abstract

This paper reports the effects of additive concentration in the casting solution on performance of asymmetric PES ultrafiltration flat sheet membranes. The membranes were prepared by phase inversion process from the casting solution containing polyethersulfone (PES) as polymer, N, N-dimethylformamide (DMF) as solvent and polyethylene glycol (PEG) of various molecular weights. The concentration of additives were varied from 5 to 25 wt% in the casting solutions. The membranes were characterized in terms of the pure water permeation, solute separation and flux. The results indicated that increased concentration of PEG 400 and PEG 600 in casting solution increased pure water permeation. It is observed that when higher concentration of PEG 200 was added in the casting solution, pure water permeation decreased significantly. As concentration of PEG 400 and PEG 600 in casting solution is increased, solute separation gradually decreases and flux increased. However, when PEG 200 concentration is increased in the casting solution, the solute separation increased significantly while flux decreased. The morphology of the membranes changed with different concentration of additive added. Experimental results revealed that different molecular weights and concentration of additives greatly influenced the performance of PES ultrafiltration flat sheet membranes.

Keywords: Concentration, polyethersulfone, ultrafiltration, polyethylene glycol, phase inversion

Introduction

Currently, ultrafiltration has become an active research area in membrane technology. A common technique for the preparation of asymmetric ultrafiltration membranes is the phase inversion method [1]. The production of flat sheet asymmetric ultrafiltration membrane includes four components which are polymer, solvent, non-solvent and additive. Additive plays a crucial role to adjust the membrane properties. The effect of different types of additives on membrane morphology and their performance have been investigated by many researchers. Non-solvent additives such as methanol, ethanol, n-propanol, diethlene glycol and deionized water were used to prepare polyethersulfone hollow fiber membranes [2-3]. The effect of non-solvent additives on solute separation of the membranes were studied and they found that PWP were increased while rejection rates were lowered as concentration of additives increased. They reported that pore sizes of the PES membranes were controlled by adjusting the concentration of additives added in casting solution.

Other researchers studied the effect of using different polyvinylpyrrolidone (PVP) such as PVP K10, PVP K30, PVP K90 and PVP K360 on performance of PES membranes. [4-8]. The role of PVP as additive in the phase inversion process have been reported where the phase-separation mechanism occurs by spinodal decomposition to form the skin and microporous sublayer [5]. Works done using PEG as additives have been reported but only using PEG 400 in PES polymer solution with concentration range from 37 to 64 wt. % [9]. It was observed that PEG 400 could be added to the casting solution in large amounts without causing phase separation. The study showed that PEG 400 can be used very well as a polymeric additive to increase the polymer dope viscosity and to enhance the pore interconnectivity when added in appropriate amounts. They reported that PEG 400 will react as macrovoid suppressor and give the membrane a hydrophilic character.

PEG 600 has been used to prepare cellulose acetate/epoxy resin blend ultrafiltration membranes [10]. They investigated the effect of concentration of PEG 600 as additive on pure water permeation performance, membranes compaction, pure water flux, water content and membrane hydraulic resistant [11]. They reported that concentration of additive greatly influenced the characteristics of cellulose acetate membranes. Other researchers investigated on the effect of PEG 200 on the formation of polyetherimide (PEI) asymmetric membrane[12]. They studied the influence of aqueous solvent mixture on performance of polyetherimide membranes. They reported that small molecular weights of PEG such as PEG 200 and PEG 400 work as pore reducing agent for PEI membranes. On the other hand, polyethylene glycols with molecular of 600, 2000, 6000 and 12,000 Dalton have been used as additives to control the thermodynamics and kinetics in casting system of polysulfone (Psf) membranes [13]. They indicated that viscosity of dope solution increased with molecular weights of additives. Besides, some researchers reported that PEG was used to improve membrane selectivity being hydrophilic in character and as a pore forming agent [13-14].

However, from literature there is yet any report regarding the effect of PEG 200 and PEG 600 on the performance of PES ultrafiltration membranes. Thus, this study aims to study the effect of using PEG of different molecular weights namely as PEG 200, PEG 400 and PEG 600 as additives for PES ultrafiltration flat sheet membranes. Polyethersulfone (PES) has been used as membrane material due to its excellent chemical resistant, good thermal stability and mechanical properties compared to polysulfone (Psf). Polyethersulfone is more suitable for liquid separation while polysulfone has advantages of gas separation and the application of higher pressures [1]. The effect of concentration of PEG with different molecular weights on pure water permeation, solute separation, flux and membranes morphology were investigated and discussed in detailed.

Approach and Methods

Materials

Polyethersulfone (PES) supplied by BASF was used as polymer in the preparation of membrane casting solution. N, N-dimethylformamide (DMF) purchased from Labscan Asia Co. Ltd was used as the solvent without further purification. Polyethylene glycols with molecular weight of 200, 400 and 600 Daltons supplied by Merck were used as additives. Polyethylene glycol 10,000 Dalton (PEG 10kDa) purchased from Fluka was used as solute. Feed solution was prepared using distilled water. Other chemicals were sodium iodide (KI) purchased from SureChe Products Ltd, barium chloride ($BACl_2$) from Labguard, iodin (I_2) from Emory and hydrochloric acid (HCl) from Merck.

Membrane preparation

Dope solutions prepared consist of different additives such as PEG 200, PEG 400 and PEG 600. Before using, polyethersulfone was dried in an oven with air circulation at 80°C for 24 hours to remove moisture. Dope solution was prepared by dissolving polyethersulfone in N, N-dimethylformamide and stirred for several hours. Then, additive was subsequently added with continuous stirring and heated at 80°C until solution is completely dissolved and homogeneous. The resultant polymer solution was kept in a glass bottle and air bubbles in the casting solutions were reduced by ultrasonification process for several hours. The various dope solution were prepared by changing different concentration of additives.

Membrane casting

The dope solution was casted on a clean glass plate using a casting knife. Immediately after casting the glass plate with the casted film was dipped into the distilled water at room temperature. Phase inversion starts and after few minutes a thin polymeric film separated out from the glass. The membranes were kept in distilled water until membrane evaluation. All flat sheet membranes were visually inspected for defects and good areas were chosen for membranes evaluation.

Ultrafiltration experiments

Ultrafiltration experiments were run using a stainless steel cross flow test cell. Membrane sample with area of 2.0×10^{-3} m^2 was placed in test cell with the active skin layer facing the incoming feed. The membrane was run for pure water permeability experiments using distilled water. Then, solute separation experiments were conducted using aqueous solution of polyethylene glycol 10,000 Dalton (PEG 10kDa) with concentration of 1000 ppm. System was thoroughly flushed with distilled water between runs of different membranes. Permeate was collected and the volume was measured. The concentration of feed and permeate solutions were determined using the following method [15] for membranes characterization.

Membrane performance evaluation

Membrane performances were characterized in terms of pure water permeation, solute separation and flux. Pure water permeation (PWP) for PES ultrafiltration membrane was calculated from the equation:

$$PWP = (Q / A \times t) \quad (1)$$

where Q is volume of the permeate (l), A = membrane surface area (m^2) and t is permeation time (hour). The solute separation of ultrafiltration membrane was given by:

$$R\ (\%) = [1 - (C_p/C_f)] \times 100 \quad (2)$$

where C_p is solute concentration in permeate stream and C_f is solute concentration in feed stream. The flux of the membrane is obtained by:

$$J = V/(A \times \Delta t) \quad (3)$$

where V is volume of permeate (l), A is membrane surface area (m^2) and Δt is permeation time (hour)

Results and discussion

Pure water permeation

Concentration influence of polyethylene glycols with different molecular weights varied from 5 to 25 wt% concentration in casting solution on PES ultrafiltration membrane performance were studied. The membranes were characterized on pure water permeation, solute separation and flux. Figure 1 shows the pure water permeation for PES ultrafiltration membranes change with different additive concentrations.

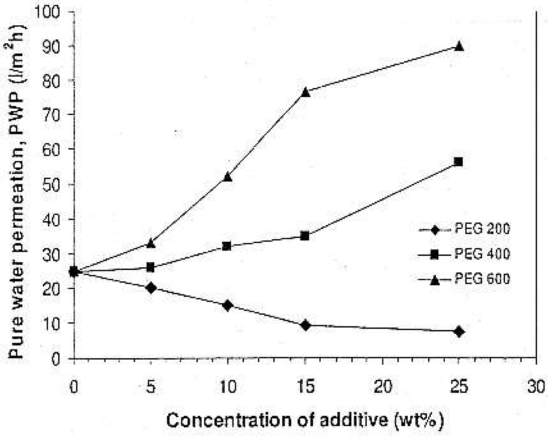

Figure 1 - The changes of pure water permeation with the concentration of additives

PES membrane without additive exhibits pure water permeation of 25.0 $lm^{-2}h^{-1}$. It is observed that as higher concentration of PEG 400 added in the casting solution, pure water permeation slightly increased. Pure water permeation gradually increases as higher concentration of PEG 600 is added in casting solution. Maximum value for pure water permeation is 90.0 $lm^{-2}h^{-1}$ at 25 wt% PEG 600 concentration. However, pure water permeation decreases linearly as concentration of PEG 200 is increased from 5 to 25 wt% concentration. It is found that at 5, 10 and 15 wt% concentration of PEG 200 in casting solution, pure water permeation is 20.1, 15.2 and 9.4 $lm^{-2}h^{-1}$ respectively. At 25 wt% concentration of PEG 200 added, pure water permeation gradually decrease to 7.4 $lm^{-2}h^{-1}$.

Solute separation and flux

The performances of solute separation and flux change with concentration of additives are shown in figure 2 and 3 respectively. PES membrane without additive exhibits 60.0% solute separation and 19.1 $lm^{-2}h^{-1}$ flux. It is observed that solute separation gradually decreased while flux increased as higher concentration of PEG 400 and PEG 600 are added. At 5 wt% concentration of PEG 600 added, solute separation is 54.0%. As the concentration of PEG 600 increased to 25 wt%, , solute separation gradually decrease to 35.2%. PES ultrafiltration membrane with PEG 400 as additive behaves in a similar manner to those containing PEG 600. At 5 wt% concentration of PEG 400 added, solute separation is 59.2%. At 25 wt% concentration of PEG 400 added, solute separation decreased to 43.0%. Maximum value for flux is 63.0 $lm^{-2}h^{-1}$ at 25 wt% concentration of PEG 600 added in casting solution. In contrast, solute separation linearly increase while flux decrease with concentration of PEG 200 from 5 to 25 wt%. Maximum value for solute separation is 91.1% at 25 wt% concentration PEG 200. It is interesting to note that the effet of PEG 400 in this study is different from those reported by Kim and Lee on PEI membranes. They reported that PEG 400 act as a pore reducing agent to PEI membranes where flux rate decreased and rejection rate increased compared to PEI membrane without additive [12]. However, in this study, it is observed that PEG 400 acts as a pore forming agent that increased flux and decreased solute separation of PES ultrafiltration flat sheet membranes. Unlike PEG 400, PEG 200 has the tendency to behave as the pore reducing agent on PES ultrafiltration membrane indicating by the improved in solute separation. Experimental results revealed that the concentration of additives with different molecular weights affect the pore size of the PES ultrafiltration membranes.

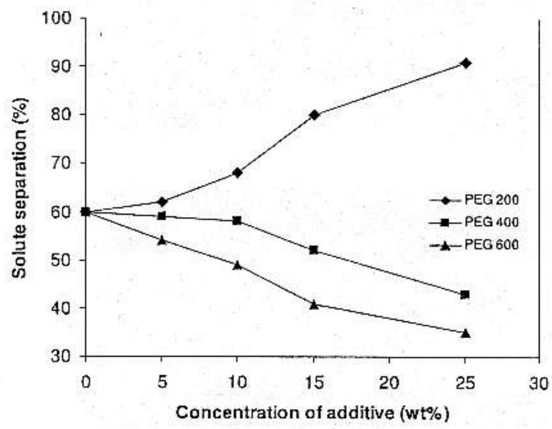

Figure 2 - The changes of solute separation with the concentration of additives using PEG 10kDa solution.

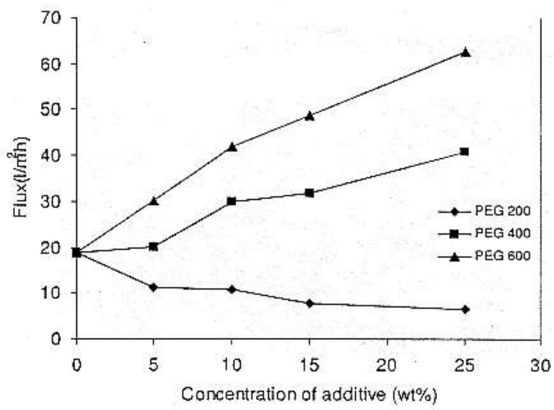

Figure 3 - The changes of flux rates with the concentration of additives using PEG 10kDa solution.

Scanning electron microscope observation

It is important to investigate on how the membrane morphology played a crucial role on performance of the membranes. In general, the SEM images indicated that the membranes have asymmetrical structure with a skin layer at the top, intermediate layer and a bottom layer. A finger like structure is found in all the skin layer of ultrafiltration membranes followed by macrovoids. From figure 4a, b and c, it seems that PEG concentration affects the morphology of PES ultrafiltraton membranes.

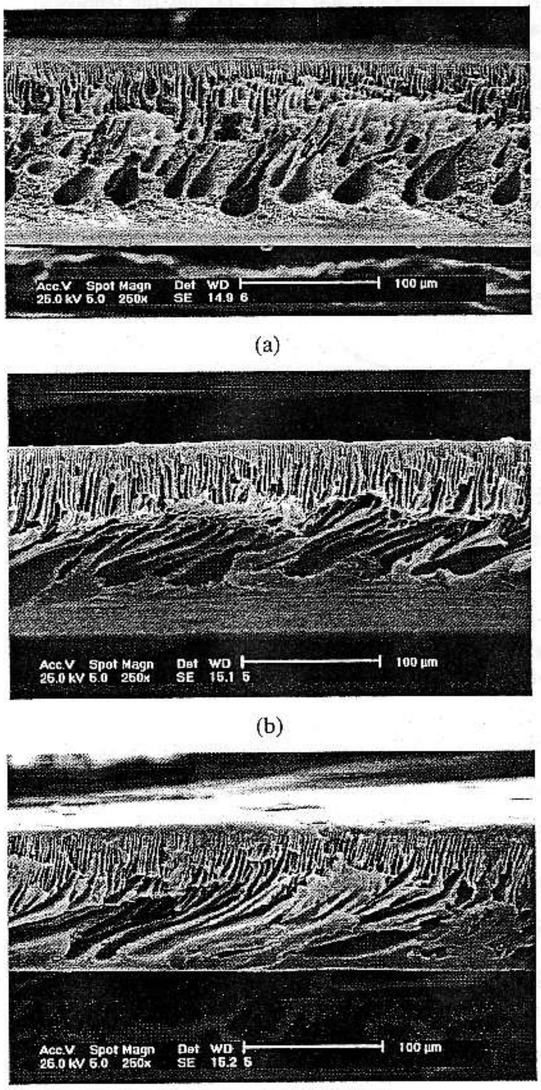

Figure 4 - Effect of concentration of PEG 600 on membrane morphology with: (a) 5 % , (b) 10% (c) 25% additive

It is obvious that on increasing PEG 600 concentration, the rounded finger like structure becomes elongated and its number also increased. Besides, it is observed that the length of macrovoids gradually extended to the bottom of the membranes at higher concentration of PEG 600 resulting in more porous membranes. Increased macrovoid formation leads to decrease of the effective thickness of the dense layer due to macrovoids in the support layer. This explained the results for the flux rates obtained while solute separation decreased with increased concentration of PEG 600 in the casting solution.

Conclusion

Concentration of additives added in casting solution can control the performance of the membranes. As concentration of PEG 400 and PEG 600 is increased in the casting solution, solute separation decreased while flux increased. PES ultrafiltration flat sheet membranes with PEG 200 as additive exhibits the highest solute separation but low flux rate as compared using PEG 400 and PEG 600 as additive.

Acknowledgements

Financial support from the Ministry of Science, Technology and Environment through the IRPA funding vote no 74246 is gratefully acknowledged.

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