Influence of Shear Rate on Proteins Separation, Molecular Weight Cut-Off and Average Pore Size of Polysulfone Blend Membranes

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Abstract. Rheological factor such as shear rate during membrane fabrication process has an effect on structural properties and performance of membranes. Flat sheet asymmetric polysulfone/cellulose acetate phthalate/polyvinylpyrrolidone (PSf/CAP/PVP) blend membranes were prepared by using an automatic casting machine at different shear rates in the range of 42.0 to 210.0 s^{-1}. The blend membranes prepared at different shear rate were characterized in terms of its structural properties (molecular weight cut-off (MWCO) and average pore size) and performance (proteins separation). The results showed that increasing the shear rate from 42.0 to105 s^{-1} has decreased MWCO and average pore size of the blend membranes which then reduced protein solution permeate fluxes and increased proteins rejection of PSf/CAP/PVP blend membranes. However, further increasing the shear rate to 210.0 s^{-1} has resulted in an increase in MWCO and average pore size and consequently increased protein solution permeate flux but decreased proteins rejection.

Keywords: Shear Rate, PSf/CAP/PVP Blend Membrane, Proteins, MWCO, Average Pore Size

Introduction

Nowadays fundamental research on membrane performance has been recognized as one of the most important elements in membrane fabrication process [1,2]. Scientists recognized that the rheological condition such as shear rate during membrane fabrication process plays an important role on the membrane performance [3]. Numerous studies by researchers proved that shear rate as one of the important rheological conditions which affects membrane morphology and properties as well as their separation performance [1-4]. Recently, a few researchers reported the effects of shear rate on properties and performance of polyimide (PI), polyethersulfone (PES) and polyaniline (PAni) membranes in gas separation process [4-6]. During fabrication of these membranes, different speed of the casting knife induced the flow of membrane casting solutions at different shear rates and as a result produced membranes of different structures and characteristics which in turn affect the membrane performance.

In ultrafiltration (UF) membrane separation process, the separation performance of UF membrane solely related to the structural properties (such as pore size) of thin skin layer (top layer) of the membrane. An extensive literature survey revealed that there is no published document discussed about the effect of different shear rate on structural properties and performance of PSf/CAP/PVP blend UF membrane. In view of this, flat sheets PSf/CAP/PVP blend UF membranes were cast at different shear rates to alter the structural properties and performance of the blend membrane. The UF blend membranes were characterized in terms of MWCO and average pore size in order to investigate the role of shear rate effects on the thin skin layer of the blend membrane which in turn attributed to a variation in permeation and separation performance of proteins solution in the UF separation process.

Materials and Methods

Experimental Procedure. First, asymmetric casting solutions membranes (PSf/CAP/PVP) were prepared and these casting solutions were cast on the steel plate by using an automatic casting machine at different shear rates. Then, the cast solutions were immersed in the coagulation bath to produce flat sheet membranes. Next, the performance of these membranes was determined via proteins separation performance tests of different molecular weight of proteins. The permeation and rejection data of proteins from different membrane were investigated. Finally, the MWCO and average pore size of each PSf/CAP/PVP blend UF membranes were determined and calculated from the permeation and rejection data of proteins.

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 consists 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. [7]. These casting solutions were cast at different shear rate. Five different shear rates were employed, viz.: 42.0 s^{-1}, 52.5 s^{-1}, 70.0 s^{-1}, 105.0 s^{-1} and 210.0 s^{-1} during membrane fabrication process and the produced blend membranes were marked as PCS-1, PCS-2, PCS-3, PCS-4 and PCS-5 membranes, respectively. The membranes were fabricated via simple wet phase inversion technique using an automatic casting machine and then immersed directly into a coagulation bath for 24 h to remove excess solvent in the fabricated membranes. The prepared membranes were stored in distilled water prior usage.

Proteins Separation Performance Test. Different molecular weight of proteins was used to study membrane separation performance of each membrane. Four different molecular weight of proteins were used in this separation such as trypsin (23 kDa), pepsin (35 kDa), egg albumin, EA (44.3 kDa) and bovine serum albumin, BSA (66 kDa). Trypsin, pepsin and EA were supplied by Sigma-Aldrich, and BSA was procured from Fluka, USA. All the proteins were used as received.
For protein permeation, a single solution of protein was prepared at concentration of 500 ppm by dissolving a pre-weighed protein powder in phosphate buffer of 7.2 pH. Protein solution was filled in the dead-end cell and it was pressurized at a constant pressure of 3 bar. The volume of permeate solution of the corresponding membranes was measured and collected in a graduated glass cylinder. The protein solutions were stirred homogenously at 100 rpm to avoid concentration polarization and fouling of proteins. The absorbance of feed and permeate of proteins were analyzed by UV-Vis spectrophotometer (Hitachi U-2000) at wavelength of 280nm. From the feed and permeate concentrations, the percentage rejection of protein was calculated.

Molecular Weight Cut-off and Average Pore Size. Molecular weight cut-off (MWCO) of the PSf/CAP/PVP blend membranes were determined by the rejection studies of different molecular weights of proteins. In this study, MWCO of the blend membranes were obtained based on the lowest molecular weight of protein that was rejected at 80% in the figure of proteins rejection versus molecular weights of protein. As MWCO of the blend membranes were determined, the average pore size of blend membranes can be obtained as explained by Sarbolouki [8].

Results and Discussion

Protein Separation Performance. The role of shear rate during membrane fabrication on the performance and rejection was studied using different molecular weight of proteins. The permeate flux and rejection of each protein for PCS-1, PCS-2, PCS-3, PCS-4 and PCS-5 membranes are illustrated in Fig. 1 and Fig. 2 respectively. According to these figures, an increase in shear rate from 42.0 to 105.0 s^{-1} significantly affected the permeate flux and rejection of each protein solution. It was evident that an increase in the shear rate resulted in the decrease of permeate flux but the percentage rejection of each protein was increased. `

A further increase of shear rate to 210.0 s^{-1} increased the proteins permeate flux but reduced the percentage of proteins rejection as depicted in Fig. 1 and Fig. 2. The rejection ability of

PSf/CAP/PVP blend membranes at different shear rate towards different molecular weight of proteins follows the sequence of PCS-4 > PCS-3 > PCS-2 > PCS-5 > PCS-1. This trend shows that an increase of shear rate increased the proteins rejection until it achieved at certain shear rate then the rejection abruptly decreased. Based on these proteins separation profiles, it is evidenced that the existence of an optimum shear rate during fabrication of PSf/CAP/PVP blend membranes which induced certain degree of polymer molecular orientation at the membrane surface and consequently yield membranes with optimal rejection rates. These results are in agreement with Ismail's et al. [9] results.

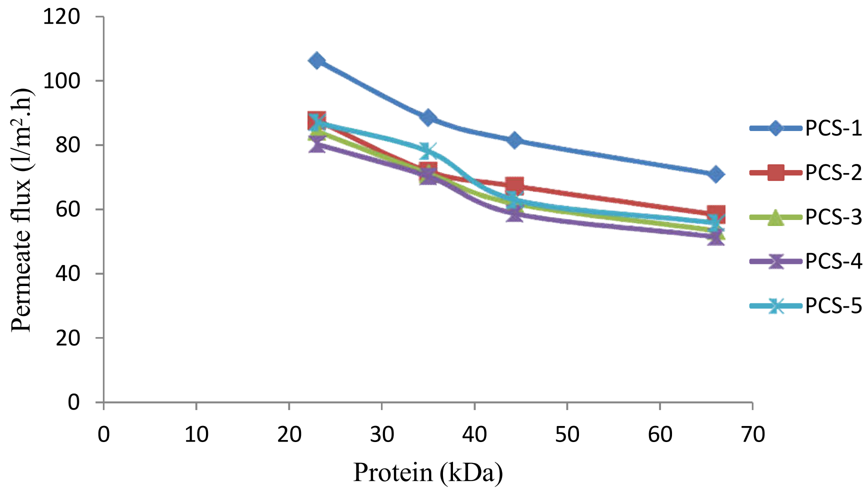

Fig. 1: Permeate fluxes of different molecular weight of proteins for PSf/CAP/PVP blend membranes fabricated at different shear rates at 3 bar.

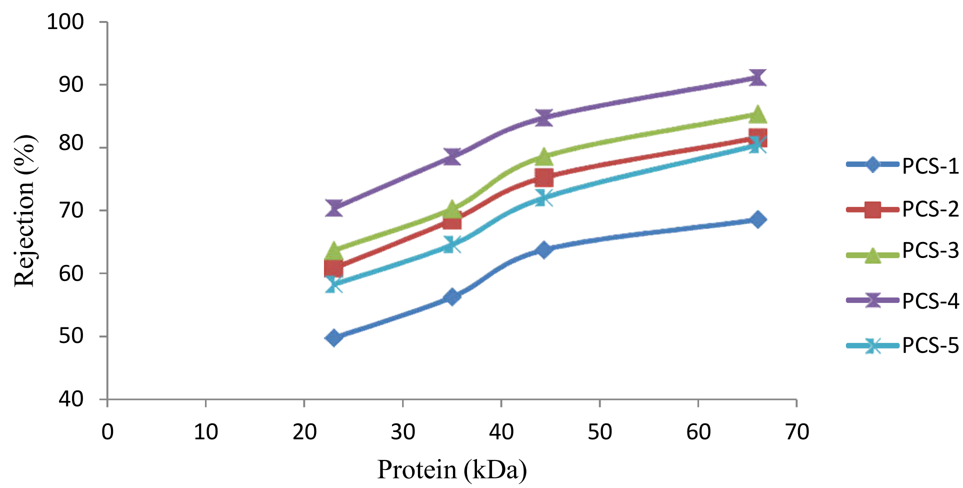

Fig. 2: Rejection of different molecular weight of proteins for PSf/CAP/PVP blend membranes fabricated at different shear rates at 3 bar.

Molecular Weight Cut-off (MWCO) and Average Pore Size. In this study, MWCO and average pore size of the PSf/CAP/PVP blend membranes fabricated at different shear rates were studied in order to investigate the role of shear rate affects on the membrane surface structural properties which in turn attributed to a variation in permeation and separation performance of protein solutions. Table 1 clearly shows that an increase of shear rate during the fabrication process of PSf/CAP/PVP blend membranes from 42.0 to 105.0 s^{-1} significantly decreased the MWCO and average pore size of the membranes surface. MWCO of upstream surface of PSf/CAP/PVP blend membranes were decreased from >66.0 to 37.0 kDa while the average pore size was reduced from >52.0 to 38.0 Å.

Wang and Chung [10] reported that there were two shear-induced mechanisms in the formation of pore sizes and porosity namely shear-induced chain orientation and packing or shear-induced deformation and transformation. If the applied shear rate was the shear-induced chain orientation and packing mechanisms, it will tighten the chains and close the package of molecules which in turn reduce pore sizes and porosity of membranes. While the shear-induced deformation and transformation will transform or deform big pore sizes and porous membranes.

Table 1: MWCO and average pore size of PSf/CAP/PVP blend membranes

Membrane	Shear rate (s^{-1})	MWCO (kDa)	Average pore size (Å)
PCS-1	42.0	> 66.0	> 52.0
PCS-2	52.5	60	49.0
PCS-3	70.0	47.5	43.0
PCS-4	105.0	37.0	38.0
PCS-5	210.0	65.0	51.5

In this study, it was evidenced from Table 1, an increase in shear rate from 42.0 to 105.0 s^{-1} decreased MWCO and average pore size of the PSf/CAP/PVP blend membranes due to the enhancement in chain orientation and entanglement as well as a formation of thick skin layers which in turn increased membrane hydraulic resistance (increased protein rejections) and consequently reduced the membrane permeability towards proteins solution permeate fluxes. This shear-induced mechanism is known as shear-induced chain orientation and packing. However an increase in shear rate beyond 105.0 s^{-1} (up to 210 s^{-1}) enhanced the MWCO and pore size of PCS-5 membranes. These results were in an agreement with the increment of permeate flux of proteins solution and the decrement of proteins rejection of the PCS-5 membrane.

Hence, it was suggested that the membrane fabricated at shear rate of 210.0 s^{-1} (PCS-5) was the shear-induced deformation and transformation in which it transformed or deformed average pore size which in turn formed a less tight and thin skin structures with high MWCO and big average pore sizes on the upstream membrane surface. So in this study it was believed the existence of an optimum shear rate which the molecular chains were oriented at the optimum orientation and beyond this optimum shear rate deteriorated the orientation of the molecular chains. Based on the experimental results, it was suggested that the optimum shear rate for preparing high performance of PSf/CAP/PVP blend UF membranes varies between 70.0 and 210.0 s^{-1}.

Conclusions

The experimental results showed that the performance of PSf/CAP/PVP blend membranes fabricated by increasing shear rate from 42.0 to 105.0 s^{-1} have resulted in a decrease in the protein permeate fluxes and an increase in proteins rejection. It was due to the increment of shear rate from 42.0 to 105.0 s^{-1} enhanced the shear-induced chain orientation and packing mechanism and consequently produced membranes with low MWCO and small average pore size. Further increasing the shear rate to 210.0 s^{-1} increased the permeability of protein solution fluxes but decreased the ability of proteins rejection. It was proved that beyond shear rate of 105.0 s^{-1}, there was the shear-induced deformation and transformation mechanism occurred at the surface layer of blend membrane which in turn formed a less tight structure with high MWCO and big average pore sizes. The results revealed that the optimum shear rate for preparing high performance of PSf/CAP/PVP blend UF membranes varies between 70.0 and 210.0 s^{-1}.

References

[1] A.F. Ismail, M.I. Mustaffar and R.M. Illias, M.S. Abdullah: Sep. Purif. Technol. Vol. 49 (2006), p. 10

[2] A. Idris, A.F. Ismail, M. Noorhayati and S.J. Shilton: J. Membr. Sci. Vol. 213 (2003), p. 45

[3] A.F. Ismail, A.R. Hassan and N.B. Cheer: Songklanakrin J. Sci. Technol. Vol. 24 (2004), p. 879

[4] T.D. Kusworo, A.F. Ismail, A. Mustafa and T. Matsuura: Sep. and Purif. Technol. Vol. 61 (2008), p. 249

[5] R. Wang and T.S. Chung: J. Membr. Sci. Vol. 188 (2001), p. 29

[6] H. Hasbullah, S. Kumbharkar, A.F. Ismail and K. Li: J. Membr. Sci. Vol. 366 (2011), p. 116

[7] A. Ali, R.M. Yunus, M. Awang and A. Johari, R. Mat: Appl. Mech. Mater. Vol. 493 (2014), p. 640

[8] M.N. Sarbolouki: Sep. Sci. Technol. Vol. 17(2) (1982), p. 381

[9] A.F. Ismail, R. Norida, W.A.W. Abdul Rahman, T. Matsuura, and S.A. Hashemifard: Desalination. Vol. 273 (2011), p. 93

[10] R. Wang and T.S. Chung: J. Membr. Sci. Vol. 188 (2001), p. 29