A Study of Fouling in Egg-white Concentration by Ultrafiltration with Tubular Module

Nam-Seok Choi[1], In-Chul Kim[1], Tae-Hyun Bae[1], Jong-Ho Kim[2], and Tae-Moon Tak[1,†]

[1]School of Biological Resources and Materials Engineering, College of Agriculture Life Sciences, Seoul
National University, Suwon 441-744, South Korea
[2]Department of Fiber Engineering, Sangju University, Sangju, South Korea

Abstract : Polyethersulfone (PES) and cellulose acetate (CA) ultrafiltration (UF) membranes having different molecular weight cut-off values were prepared by immersion precipitation method by changing the compositions of casting solution. Egg white solution was concentrated to volume concentration ratio 4 in tubular UF with membranes made of moderately hydrophobic PES and hydrophilic CA. The process parameters such as pressure and fluid velocity were controlled in order to apply successfully for egg white solution and to investigate the pressure dependency. The resistance values were measured to investigate the fouling and concentration polarization effect on membrane performance. During concentration of egg white solution by UF, the fouling layer appeared to contribute little resistance to flux compared to that of polarized layer.

1. Introduction

Synthetic polymeric membranes, such as those used for microfiltration (MF), ultrafiltration (UF), or reverse osmosis (RO), have gained considerable technological importance and have been found to be uniquely useful separation tools in many important applications [1-3]. The production of UF membranes requiring a finely porous selective layer on top of the membrane was also initially based on cellulose esters, and these still play an important role because of their comparatively low material price and their good compatibility with biological materials, especially

†Author for all correspondences
(e-mail : tmtak@snu.ac.kr)

proteins. Unlike MF, UF is used not only for the purification or separation of suspended or dispersed substances in mixtures but also for the removal of oligomeric or macromolecular substances from solutions. Virtually almost UF membranes are asymmetric porous membranes. For instance, a typical UF membrane is manufactured from immersion precipitation method. Polysulfone (PSf) or polyethersulfone (PES) is a polymer extensively studied for membrane application because of its chemical resistance.

Concentration of egg-white solution, like any other food product, involves removal of water in order to reduce package, storage and transport costs. Membrane process is gradually emerging as a powerful concentration method due to several advantages such as minimum thermal

damage, lower energy consumption and lower capital equipment costs [4-6]. In UF process, flux and rejection rate are important performance indices. Operating parameters like transmembrane pressure, temperature, flow rate and feed concentration are important factors controlling flux. Especially, in order to lessen the fouling which reduces productivity, and potentially shortens membrane life, it was reported that operating in the pressure-independent region was useful for reducing fouling [7]. The phenomenon of flux decline was observed to be significant [8]. Membrane fouling has been the subject of interest of membrane researchers [9,10]. An extensive review was given on fouling in UF processes. In most studies, attempts have been made to relate fouling on flux decline resulting from an increase in flow resistances [11,12].

Moreover, with increasing the flow rate, the gel layer on the membrane surface can be broken by shear. Rejection, on the other hand, can be controlled by the pore size of the membrane and, to a lesser extent, by the operating parameters [11].

The objectives of this study were to investigate the ability of UF for concentrating the egg-white solution by tubular module and to study the effects of parameters on fouling on hydrophobic and hydrophilic membrane based on a model of resistance-in series concept [13,14].

2. Experimental

2.1. Membranes

The membranes having different molecular weight cut-off (MWCO) values were prepared by the typical phase inversion methods. Polyethersulfone (PES, BASF) as a hydrophobic polymeric material and polyvinylpyrrolidone (PVP pk-30, Aldrich) as an additive (pore forming agent) were dissolved in N-methyl-2-pyrrolidone (NMP, Aldrich), and then cast on polyester non-woven fabric. The nascent membrane was coagulated in deionized ice-cold water after evaporating at temperature, 25 ± 1℃ and relative humidity, $65 \pm 5\%$ for 30 sec. Cellulose acetate (CA, EASTMAN KODAK) as a hydrophilic polymeric material was dissolved in

solvent mixture of NMP and acetone. CA membrane was prepared in the same way as in the PES membrane preparation procedure. Membranes were prepared in the form of plate-and frame and tubular.

2.2. Egg-white Solution

Egg-white of fresh eggs with no water dilution were separated and used as a feed for the ultrafiltration experiment. The egg-white solution for our experiment was consisted of protein (10 wt%), carbohydrate (1.2 wt%), mineral (0.3 wt%), ash (0.5 wt%) and water (88 wt%). Density of feed, retentate and permeate was 1.0 g/mL.

2.3. Ultrafiltration Process

The membranes were compacted in an ultrafiltration cell for 3 hr at pressure, 2 kg/cm²; flow rate, 2.5 L/min; temperature, 25℃. Then, the pressure was lowered to 1 Kg/cm² and the pure water flux was measured. The solute rejection rate was measured with 1000 ppm aqueous solution of the poly(ethylene glycol) having different molecular weight. The protein, water and ion contents of the permeate and the retentate were measured with Kjeldahl protein/nitrogen analyzer (2300 Kjeltec analyzer unit), water contents analyzer (Denver instrument Mark II HP) and Ion chromatograph (Shimazu Chromatograph HIC/10A), respectively.

Tubular membranes having a nominal molecular weight cut-off (MWCO) 50 kDa of PES and CA were prepared. Tubular membrane was packed into modules. A module contained 6 pieces of tubular membrane of 120 cm long and 1cm wide. Two membranes were nominated with PES 50000 and CA 50000, respectively. A tubular system is useful for concentrating fluids of high viscosity without permanent fouling. The feed solution for ultrafiltration operation was maintained a temperature of 25 ± 2℃. The operating feed velocity was 1.8m/sec. The testing pressure was controlled to 2 kg/cm². The volume concentration ratio (VCR) concept which is initial feed volume divided by retentate volume was used. The volume of the initial feed was 100 L.

2.4. Analysis of Resistances

In order to compare the fouling of hydrophobic PES and hydrophilic CA membrane during the ultrafiltration of egg-white solution, the resistance values of the membranes having a nominal MWCO of 50 kDa were measured with Amicon stirred cell. The resistances were evaluated from the following resistance-in-series model.

$$J_v = \Delta P/\mu R_t,$$

Where J_v is the permeation flux of solution (mS^{-1}), P the transmembrane pressure difference (kPa), μ the viscosity of solution (PaS^{-1}) and R_t the total resistance (m^{-1}). In this study R_t is defined as;

$$R_t = R_m + R_p + R_f,$$

Where R_m is the resistance of clean membrane, R_p the resistance of polarized layer and R_f fouling resistance.

R_m is the resistance of clean membrane that can be calculated from pure water flux data (J_w)

$$J_w = \Delta P/\mu_w R_m,$$

Where μ_w is the viscosity of pure water $(Pa\ S^{-1})$. After experiment of J_v, the membrane was cleaned by circulating distilled water in order to remove the polarized layer resistance (R_p). The water flux measured after cleaning is; $J_w' = \Delta P/\mu_w (R_m + R_f)$.

3. Results and Discussion

3.1. Membrane Performance

The pore size of membrane can be controlled by changing the compositions of the casting solution and the coagulation bath. In economical aspect, changing the composition of the casting solution is better. In case of polyethersulfone (PES) which is moderately hydrophobic polymer, the concentration of the polymer (PES) and a second pore-forming polymer (PVP) was varied. By changing two parameters, PES membrane having the molecular weight cut-off (MWCO) values in the range of 20,000 to 50,000 could be prepared. However, in case of cellulose acetate (CA), which is more hydrophilic than PES, solvent mixture (NMP and acetone) was used instead of only one solvent. If only NMP was used as a solvent, the MWCO was too large (about a few 100 kDa). And in case of acetone, the MWCO became too small (about a few 1 kDa). This is due to the high volatility of acetone and low miscibility with water. Therefore, the ratio of NMP to acetone was changed. The MWCO of CA membrane was in the range of 20 kDa to 80 kDa. Table 1 shows the compositions of casting solutions for preparing membranes having different MWCOs. Table 2 shows the performance of PES and CA membrane having MWCO 50 kDa. Although two membranes have

Table 1. Compositions of PES and CA Casting Solution for Membrane Preparation

Code	PES	CA	NMP	Acetone	PVP 40000
PES 20000	22.9		72.5		4.6
PES 35000	21.4		67.9		10.7
PES 50000	18.2		72.7		9.1
CA 20000		20	30	50	
CA 35000		19.6	19.6	58.8	20
CA 50000		19.2	28.8	48.1	3.9
CA 80000		18.9	28.3	47.2	5.6

Table 2. Membrane Performance

Code	Flux (l/m^2hr)[1]	Solute rejection rate (%)[2]
PES 50000	167	86
CA 50000	82	88

1) Pressure: 1 Kg/cm^2
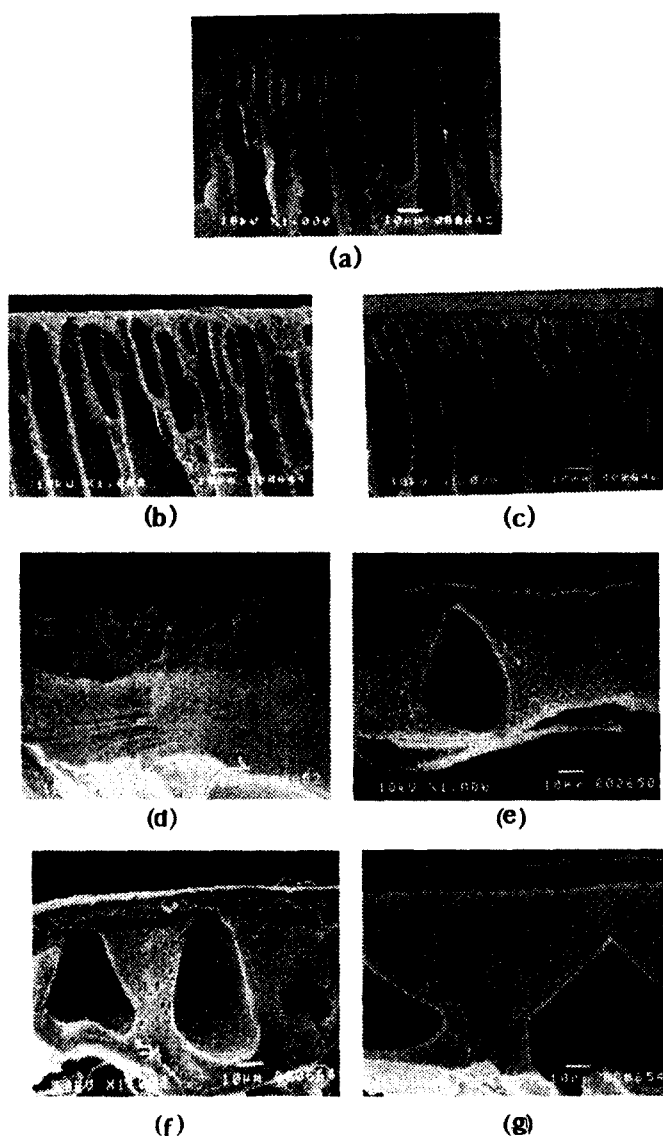2) 1000 ppm of PEG 50000 aqueous solution

Fig. 1. SEM photographs of PES and CA membranes.
(a) PES 20000 (b) PES 35000 (c) PES 50000 (d) CA 20000 (e) CA 35000 (f) CA 50000 and (g) CA 80000.

similar rejection rate to PEG 50,000, the flux of CA membrane is lower than PES membrane. This is due to lower porosity of CA membrane than PES membrane. When preparing CA membrane, acetone solvent having low boiling point was used. Before immersing nascent membrane, acetone can be easily evaporated in the air. During evaporation of acetone CA polymer can be aggregated and formed denser skin layer. Further,

the mutual miscibility of acetone with water is lower than that of NMP. In general, it is to be expected that membrane from casting solution consisted of good miscibility solvent with coagulant is porous [1,2]. This can be explained in SEM photographs (Figure 1). In case of hydrophobic PES membrane, finger-like cross-section structure was shown. With increasing the MWCO of membrane, the size of the finger
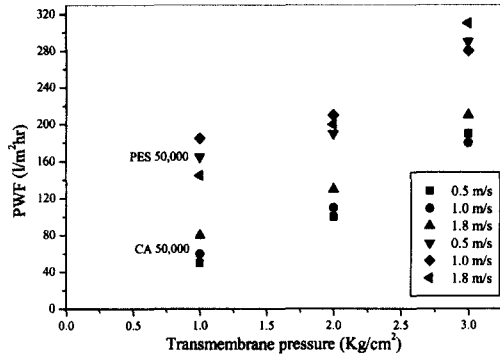
Fig. 2. Pure water flux for two tubular modules as function of transmembrane pressure and fluid velocity; operation temperature: 25℃.

Fig. 3. Ultrafiltration of egg-white solution in tubular module; operating temperature: 25±1℃, closed part and straight line: PES 50000, open part and dotted line: CA 50000.

became bigger and the distance of incipient finger near (thinner skin layer). However, in case of hydrophilic CA membrane, the cross-section shape of CA membrane was sponge-like. The numbers of fingers were very small, and instead the size became very bigger. Further, the skin layer became very thicker. This is why the flux of CA membrane is smaller than PES membrane.

Pure water flux of tubular module prepared from PES and CA polymer is shown in Figure 2. Both membranes have the same flux patterns. When system is operated in the pressure-dependent region, flux was proportional to operating pressure, but independent of flow velocity. These results were the same with Cheryan and Chiang's experiments [7,8]. However, when system is operated in the mass transfer-controlled region, with increasing the cross-flow velocity turbulence will be obtained. This turbulence in the feed channel sweeps away the accumulated solute on the membrane surface, and the resulting flux is increased, as can be seen in Figure 3. In other words, flux initially increased linearly with pressure and then became independent of pressure. Chiang and Cheryan have explained this as
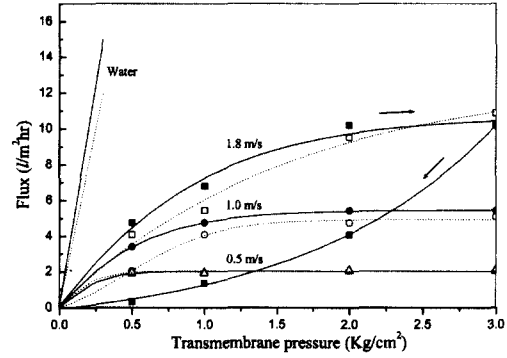
concentration polarization, which is the build-up of rejected protein molecules on the membrane surface. In other words, initially at low pressure, shear and lift forces were sufficient to minimize particle deposition, and the flux increased linearly with pressure. As soon as the particles started to deposit on the membranes, the flux decreased. Further solute build-up resulted in a denser solute layer. When no more solute molecules can be accommodated because of the closely packed arrangement and restricted mobility of solute molecules, a steady-state (a rate of convective transport of solute to the membrane and back-transport of the solute into the bulk phase balanced.) is reached, and resulting flux is constant with increasing transmembrane pressure when pressure was decreased, high shear forces could not remove the solutes from the gel layer, resulting in the hysteresis effect shown in Figure 3.

3.2. Concentration of Egg-white Solution

Table 3 shows the fractionation data of egg-white solution. Egg-white solution was concentrated to VCR 4. Proteins of egg-white solution

Table 3. Ultrafiltration of Egg-white Solution

| Volume (L)	VCR	Protein %w/v	Protein kg	Carbohydrate %w/v	Carbohydrate kg	Ash %w/v	Ash kg	Mineral %w/v	Mineral kg	Total solids %w/v	Total solids kg	Protein content of solids (% d.b.)
100	1	10.0	10.0	1.2	1.2	0.50	0.50	0.30	0.30	12.0	12.0	83.3
50	2	18.4	9.2	1.2	0.60	0.60	0.30	0.30	0.15	20.5	10.3	89.8
25	4	36.8	9.0	1.2	0.30	0.72	0.18	0.30	0.08	39.0	9.6	94.5

Table 4. Resistances Obtained from Ultrafiltration of Egg-white Solution by PES and CA Membranes for 9 hr. Operating Conditions: 25°C, 2 kg/cm², Cross-flow Velocity 1.8 m/sec

Code	Resistance (10^{12}m^{-1})				Normalized resistance(-)		
	R_m	R_p	R_f	R_t	R_m/R_t	R_p/R_t	R_f/R_t
RES 50000	1.53	150.68	3.79	156	0.0060	0.97	0.024
CA 50000	5.85	132.98	1.17	140	0.040	0.95	0.010

consisted of ovalbumin (50% of relative amount, MW 45000Da) ovomucoid (10%, MW 28000Da), conalbumin (15%, MW 87000 Da) and lysozyme (2-4%, MW 14000Da) could be retained to 92% at our operating conditions because of self-forming dynamic membrane on membrane surface. Carbohydrate and mineral were completely transported through the membrane. And the rejection rate of ash was about 22%. From these experimental data, the contents of components of retentate could be expected. And more, the expected values which is followed by Cheryan's derivation could be compared to our experimental data. As can be seen from Table 3, the calculated values are well-defined with the experimental data. When egg-white solution was concentrated to VCR 4, the content of protein can be increased to 94.5%.

3.2. Membrane Fouling

Fouling can be occurred by the complicated physicochemical interactions of feed components. Especially, proteins can be a major foulant in membrane processing, considering the multiplicity of functional groups, the charge density within protein molecules, the varying degrees of hydrophobicity, and the complex secondary and tertiary structure that allows a protein to interact with membrane. Membrane material is also an important factor to fouling. In general, hydrophilic CA membrane has been known to be fouled less compared to other hydrophobic polymeric membranes due to smooth and uniform surface of CA membrane. Figure 4 also confirms that the CA membrane fouls less compared to PES membrane. During concentration, flux decrease of CA membrane was moderate, which means the membrane is not fouled severely. However, flux decrease of PES membrane is considerable, which means the
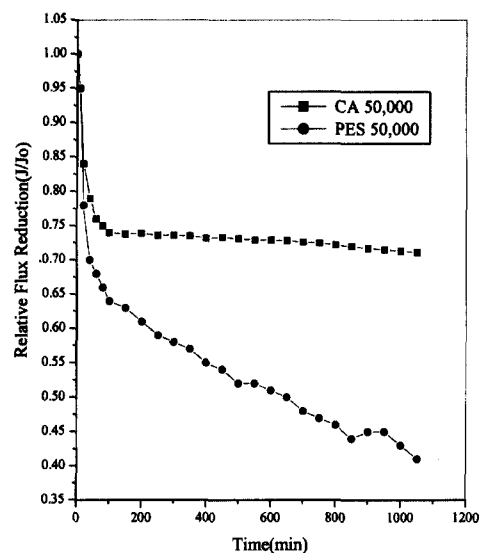
Fig. 4. Fouling of PES and CA membranes in tubular modules by egg-white solution: operating temperature: 25±1°C, operating pressure: 2 kg/cm², flow rate: 1.8 m/sec.

membrane is fouled severely. Table 4 compares R_m, R_p, R_f, and R_t obtained from ultrafiltration of egg-white solution by PES and CA membrane using the same operation conditions. The polarized layer resistance R_p for both membranes is the major contribution to total resistance R_t. This means that in order to increase the concentration efficiency high flow velocity is needed to reduce the concentration polarization layer thickness. Moreover, compared to fouling resistance R_f, which is the index of fouling susceptibility hydrophobic PES 50000 membrane can be fouled more than hydrophilic CA 50000 membrane.

4. Conclusion

The molecular weight cut-off values of polyethersulfone (PES) and cellulose acetate (CA)

membranes were controlled by changing the compositions of casting solutions. The flux of CA membrane was lower than that of PES membrane due to acetone evaporation and low miscibility with water. The PES membrane has finger-like cross-section and the CA membrane has sponge-like structure. The results of this study have demonstrated that the ultrafiltration with tubular module is feasible for concentration of egg-white solution. With increasing the fluid velocity pressure-controlled region was widened. And PES membrane, which is hydrophobic, was more sensitive to fouling than a hydrophilic CA membrane by egg-white protein. The resistance values were measured using a resistance-in-series approach. The polarized layer resistance was the key contribution to the total resistance. Compared to fouling resistance R_f, a hydrophobic PES membrane can be fouled easily than a hydrophilic CA membrane.

Acknowledgment

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